

CHEMICAL EVOLUTION OF WATERS IN THE LANSING-KANSAS CITY GROUPS
IN WESTERN KANSAS

by

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CONTENTS

	Page
Introduction - - - - -	1
Statement of problem - - - - -	1
Study area - - - - -	2
Previous work - - - - -	2
Sample collection - - - - -	5
Analytical Procedure - - - - -	6
Major chemistry - - - - -	6
Isotopic determination - - - - -	10
X-ray diffraction - - - - -	11
Petrography - - - - -	12
Geology of the study area - - - - -	13
Regional geology - - - - -	13
Lansing-Kansas City stratigraphy of the study area - - -	18
Classification of zones - - - - -	27
Diagenesis of Lansing-Kansas City strata - - - - -	27
Results - - - - -	30
Chemical data of the waters - - - - -	30
Isotopic data of the waters - - - - -	48
Oxygen and hydrogen isotopic data - - - - -	48
Strontium isotopic data - - - - -	50
Petrography - - - - -	55
Carbonates - - - - -	55
Shales - - - - -	56
Discussion - - - - -	57

CONTENTS (con't.)

	Page
Potentiometric configuration - - - - -	57
Major chemistry - - - - -	59
Sodium - - - - -	60
Bromide - - - - -	64
Magnesium, calcium, and strontium - - - - -	65
Lithium - - - - -	68
Potassium - - - - -	69
Rubidium - - - - -	71
Sulfate - - - - -	72
Bicarbonate - - - - -	76
Iodide - - - - -	76
Oxygen and hydrogen isotopes of the oil-field waters - - - - -	77
Strontium isotopes - - - - -	83
Spatial distribution of water composition - - - - -	88
Conclusion - - - - -	90
Acknowledgements - - - - -	92
References cited - - - - -	93

ILLUSTRATIONS

Figure	Page
1. Location of study area - - - - -	3
2. Plot of wells from which water and core samples were collected - - - - -	4
3. Major structural features in Kansas - - - - -	14

ILLUSTRATIONS (cont'd)

Figure		Page
4.	Generalized geologic cross section through study area - - - - -	15
5.	Missourian (late Pennsylvanian) paleogeographic map of western Kansas and adjacent areas - - - - -	17
6.	Generalized stratigraphic column of Pennsylvanian rocks in western Kansas - - - - -	19
7.	Formal member and formation nomenclature of the Lansing-Kansas City Groups in Kansas - - - - -	20
8.	East-west cross section of the Lansing-Kansas City Groups through the study area - - - - -	21
9.	North-south cross section of the Lansing-Kansas City Groups through the study area - - - - -	22
10.	Basic sequence of Midcontinent Pennsylvanian "Kansas cyclothem" - - - - -	24
11.	Stratigraphic classification schemes for the Lansing- Kansas City Groups - - - - -	28
12.	Comparison of concentrations in Lansing-Kansas City oil-field waters, western Kansas with evaporating sea water. Solid line represents sea water evaporation curve: a) Cl vs Na and b) CL vs Li - - - - -	38
13.	Comparison of concentrations in Lansing-Kansas City oil-field waters, western Kansas, by production zone, with evaporating sea water. Solid line represents sea	

ILLUSTRATIONS (cont'd)

Figure	Page
water evaporation curve: a) Cl vs Na, b) Cl vs Li, and c) Cl vs K - - - - -	39
14. Spatial distribution of concentrations over the study area: a) Na X 1,000 and b) K X 10 - - - - -	40
15. Comparison of concentrations in Lansing-Kansas City oil-field waters, western Kansas with evaporating sea water. Solid line represents sea water evaporation curve: a) Cl vs Ca, b) Cl vs Sr, and c) Cl vs Mg - - - - -	41
16. Comparison of concentrations in Lansing-Kansas City oil-field waters, western Kansas, by production zone, with evaporating sea water. Solid line represents sea water evaporation curve: a) Cl vs Ca, b) Cl vs Sr, and c) Cl vs Mg - - - - -	42
17. Spatial distribution of concentrations over the study area: a) Ca X 100, b) Sr, and c) Mg X 10 - - - - -	44
18. Comparison of concentrations in Lansing-Kansas City oil-field waters, western Kansas with evaporating sea water. Solid line represents sea water evaporation curve: a) Cl vs K and b) Cl vs Rb - - - - -	46
19. Comparison of concentrations in Lansing-Kansas City oil-field waters, western Kansas with evaporating sea water. Solid line represents sea water evaporation curve: a) Cl vs SO ₄ , b) Cl vs Br, and c) Cl vs I - - - - -	47

ILLUSTRATIONS (cont'd)

Figure	Page
20. Comparison of concentrations in Lansing-Kansas City oil-field waters, western Kansas, by production zone, with evaporating sea water. Solid line represents sea water evaporation curve: a) Cl vs I and b) Cl vs Br - - - - -	49
21. Spatial distribution of values over the study area: a) $\delta^{18}\text{O}$ and b) δD - - - - -	52
22. Spatial distribution of values over the study area: a) $^{87}\text{Sr}/^{86}\text{Sr}$, b) TDS X 1,000, and c) Bottom hole pressure - - - - -	54
23. Concentrations of a) SO_4 vs Ca and b) SO_4 vs Sr in Lansing-Kansas City oil-field waters - - - - -	73
24. Concentration of calcium and sulfate during evaporation of a solution in equilibrium with gypsum, assuming initial molar concentration of SO_4 is much greater the initial concentration of Ca, neglecting activity corrections - - - - -	75
25. Relation of δD and $\delta^{18}\text{O}$ in Lansing-Kansas City oil-field waters, western Kansas to O and D shifts exhibited during evaporation of normal sea water containing hydration waters of gypsum - - - - -	79
26. Relationships among chemical and isotopic characteristics of Lansing-Kansas City oil-field waters: a) Cl vs $^{87}\text{Sr}/^{86}\text{Sr}$ and b) $^{87}\text{Sr}/^{86}\text{Sr}$ vs $1/\text{Sr}$ - - - -	87

TABLES

Table	Page
1. Well name, operator, location, production zone, and depth of oil-field waters from the Lansing- Kansas City Groups - - - - -	7
2. Well name, operator, location, and sample depth or production zone, of cores from the Lansing- Kansas City Groups - - - - -	8
3. Major cation and TDS analyses of Lansing-Kansas City oil-field waters, western Kansas (concentrations expressed in mg/l) - - - - -	31
4. Anion analyses of Lansing-Kansas City oil-field waters, western Kansas (concentrations expressed in mg/l) - - - - -	32
5. Major cation analyses of Lansing-Kansas City oil-field waters, western Kansas (concentrations expressed in meq/l) - - - - -	33
6. Anion analyses of Lansing-Kansas City oil-field waters, western Kansas (concentrations expressed in meq/l) - - - - -	34
7. Ranges of chemical and isotopic values for the Lansing-Kansas City oil-field waters - - - - -	35
8. Stable isotopic analyses of Lansing-Kansas City oil-field waters, western Kansas (concentration expressed in per mil SMOW) - - - - -	51

TABLES (cont'd)

Table	Page
9. Strontium isotopic composition of Lansing-Kansas City oil-field waters, western Kansas - - - - -	53
10. Mineralogy of shale samples collected from the Lansing-Kansas City cores (values in percent of clay mineral fraction) - - - - -	58

INTRODUCTION

STATEMENT OF PROBLEM

The waters associated with petroleum deep within the subsurface are typically much more concentrated than sea water, which has a salinity of about 35,000 mg/l. Deep subsurface waters may originate as sea water or meteoric water that is deposited with the sediments, interstitial water in minerals expelled during compaction, or a mixture of these. The chemistry of the original water may then be modified within the subsurface by processes including: 1) evaporation, 2) mineral dissolution and precipitation, 3) ion exchange with clay minerals, 4) ultrafiltration through shale membranes, 5) biologic activities, and 6) mixing with other waters. Through these processes the waters can affect the porosity and permeability of the host rocks.

The purpose of this study was to investigate the origin and chemical evolutionary history of Lansing-Kansas City oil-field waters throughout western Kansas which, in turn, may reveal information concerning their role in diagenesis of the reservoir rocks. The variation of oil-field water chemistry from different stratigraphic zones of the Lansing-Kansas City Groups was investigated in an attempt to explore the existence and extent of hydrologic connections between the zones. This knowledge can be applied when exploring for hydrocarbons which are associated with these waters.

The Upper Pennsylvanian Lansing-Kansas City Groups are major hydrocarbon reservoirs in western Kansas. The scope of this study was to analyze the chemical, Sr isotopic, and stable isotopic compositions of oil-field waters produced from carbonate reservoir rocks of the

Lansing-Kansas City Groups in western Kansas. Some selected core samples of the reservoir rocks were analyzed for their mineralogical and chemical compositions.

STUDY AREA

The study area is composed of 21 counties located in the western one third of Kansas (Fig. 1). Samples were collected from multiple counties to obtain a regional perspective of the chemical and isotopic variation present in the Lansing-Kansas City waters (Fig. 2). Samples were collected from several stratigraphic zones in a small area between townships 14-18 south and ranges 26-31 west, near the boarder of Gove and Lane counties, to determine any chemical variation between the different producing zones within the Lansing-Kansas City Groups (Fig. 2).

The depth of production varies throughout the study area. Production is shallowest in the eastern (3,000-3,500 feet) and northern (3,500 feet) portions. The production depth increases to approximately 4,000 feet in the central region of the study area and reaches 5,000 feet near the Oklahoma boarder.

PREVIOUS WORK

Chemical and stable isotopic data has been used to determine the evolution and migration history of oil-field waters (DeSitter, 1947; Degens et al., 1964; White, 1965; Clayton et al., 1966; Rittenhouse, 1967; Hitchon et al., 1971; Kharaka et al., 1973; Kharaka and Berry, 1974; Collins, 1975; Carpenter, 1978). Strontium isotopic composition

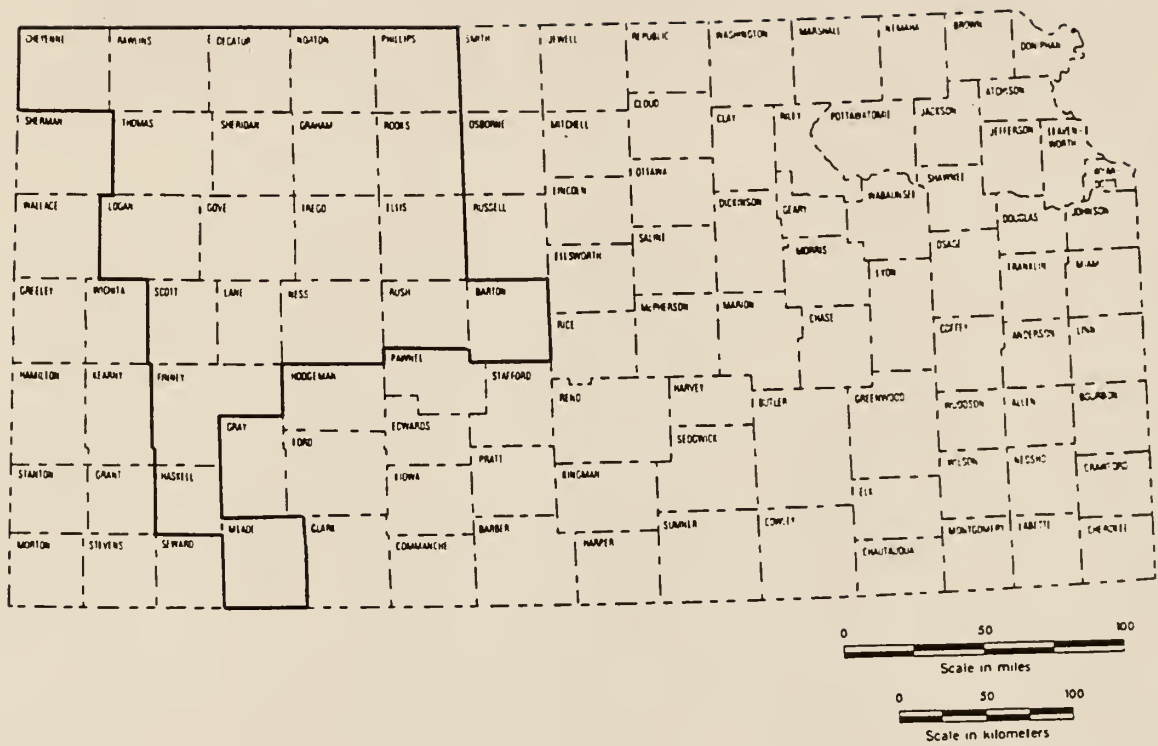


Figure 1. Location of the study area.

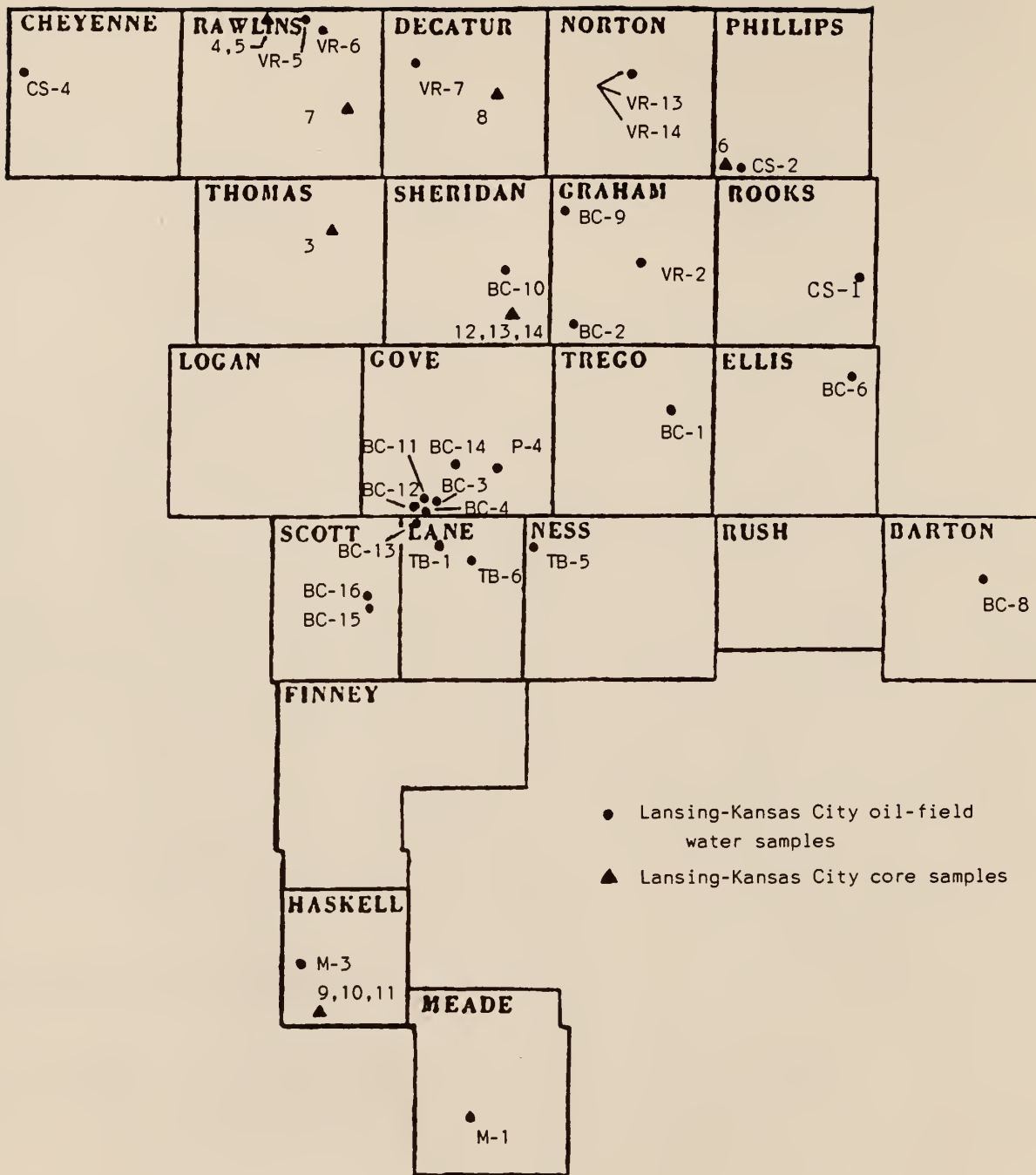


Figure 2. Plot of wells from which water and core samples were collected.

has been used to determine migration and accumulation of oil-field waters (Chaudhuri, 1978). He attributed anomalously high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in brines from Kansas and Colorado to interaction with Rb-rich clay minerals surrounding the reservoir rocks. Sunwall and Pushkar (1979), working on oil-field waters from Ohio, concluded that consistency of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios can be used to identify uncontaminated oil-field waters. Studies by Chaudhuri et al. (1983), Starinsky et al. (1983), Steuber et al. (1984), and Chaudhuri et al. (1987) have provided valuable clues to the migration paths and evolution of oil-field waters along with their diagenetic effect on the reservoir rocks.

Dingman and Angino (1969) reported the average chemical composition of waters from the Lansing-Kansas City Groups in an attempt to correlate salinity of associated water with formation depth. However, they made no attempt to reconstruct the origin or chemical evolution of the waters. Broedel (1983) and Nicastro (1983) reported chemical and isotopic data for oil-field waters from Mississippian to Lower Pennsylvanian reservoir rocks on the western flank of the Central Kansas Uplift. They attributed the chemical composition of the waters to evaporated sea water that was modified by mixing with meteoric water and by mineral-water interactions.

SAMPLE COLLECTION

Aliquots of oil and water were collected in one liter polyethelene bottles that had been soaked in a HNO_3 solution and then rinsed in distilled, demineralized water. Each was taken directly

from the well head after allowing it to flow for 30 seconds to flush out the pipe. The bottles were immediately sealed after the collection of each sample and the water was gravitatively separated from the oil. Each water was filtered through Whatman 42 Ashless paper prior to chemical and isotopic analyses. The water samples were stored in precleaned bottles. Well data for each of the oil-field waters sampled are listed in Table 1.

Several core samples of Lansing-Kansas City strata were obtained from the Kansas Geological Survey collection at Lawrence, Kansas. Samples of shale, limestone or dolostone, and vug fillings of rocks from different stratigraphic intervals and locations were obtained from the cores. Information concerning the Lansing-Kansas City core samples are listed in Table 2.

ANALYTICAL PROCEDURE

MAJOR CHEMISTRY

The oil-field waters were analyzed for their elemental contents using a Perkin-Elmer model 305B Atomic Absorption Spectrophotometer. Calcium, Mg, Na, and Sr concentrations were determined by atomic absorption. Emission spectrographic methods were used to find the K, Li, Rb, and Si content.

Cation concentrations were also determined in a second laboratory to check the accuracy of the analyses. In this second laboratory, Na, Rb, and Li analyses were done by flame emission using a Jarrell-Ash 810 Atomic Absorption Spectrophotometer while all other

Table 1. The well name, operator, location, production zone, and depth of oil-field waters from the Lansing-Kansas City Groups.

<u>Sample</u>	<u>Well Name</u>	<u>Operator</u>	<u>Legal</u>	<u>Production</u>	
				<u>Zone</u>	<u>Depth</u>
BC-1	U.S. Govt. 4	Beren Corp.	35 12S 22W	A,F	3640
BC-2	Brungardt A-4	Beren Corp.	22 10S 25W	B,F	3900
BC-3	James Mariam 1	Beren Corp.	29 15S 29W	L	4000
BC-4	Ross 1	Beren Corp.	31 15S 29W	H,K	3940
BC-6	Potter A-1	Okmar Oil	19 11S 16W	A,C	3050
BC-8	Pierano 1	Beren Corp.	31 17S 12W	B,F	3100
BC-9	Ward 1	Okmar Oil	31 6S 25W	C,D	3720
BC-10	Jerome 3	Okmar Oil	35 8S 27W	B,C,H,J	3900
BC-11	Gladys	Beren Corp.	30 15S 29W	K	3940
BC-12	Bishop	Beren Corp.	25 15S 30W	K	3980
BC-13	Lottie 2	Beren Corp.	1 16S 30W	B	3800
BC-14	Purcelle	Beren Corp.	24 14S 29W	K,L	4020
BC-15	Chance	Beren Corp.	19 18S 31W	E	4000
BC-16	Huesman	Beren Corp.	18 18S 31W	B	3950
CS-1	Dennis A-1	Cities Service	34 8S 16W	A,B,D	3120
CS-2	Kohman 3	Cities Service	35 5S 20W	A,B,D,G,M	3340
CS-4	Norhtrup A-2	Cities Service	26 2S 42W	A,J	4620
M-1	Hilst 1-36	Mesa Petroleum	36 33S 29W		4970
M-3	Clawson 1-4	Mesa Petroleum	4 29S 34W		4500
P-4	Leighton F-1	Pickeral Drilling	29 14S 27W	K	3920
TB-1	Richards 1	Thunderbird Drill.	20 16S 29W		
TB-5	Arnold 2	Thunderbird Drill.	31 16S 26W		
TB-6	Graeff 1	Thunderbird Drill.	9 17S 28W		
VR-2	Wyatt 1	Jack Bowles	23 8S 23W		3870
VR-5	Vap 1	Viking Resources	4 1S 33W	J	
VR-6	Wicke C-1	Slawson Oil	17 1S 32W		
VR-7	Mines A-2	Okmar Oil	13 2S 30W		
VR-13	Fedde	Viking Resources	33 2S 23W	D	3500
VR-14	Le Count	Viking Resources	33 2S 23W	K	3500

Table 2. The well name, operator, location, and sample depth or production zone of cores from the Lansing-Kansas City Groups.

<u>Sample</u>	<u>Well Name</u>	<u>Operator</u>	<u>Legal</u>	<u>Production Depth(ft)/Zone</u>
CARBONATES				
1	Reidel 6	Empire Drilling	06 10S 22W	3925.4
2	Smith 1	Texas Oil & Gas	30 11S 36W	4772.0
3	Knudson A	Cities Service	16 07S 32W	J-zone
4	Souчек 1	Murfin Drilling	02 01S 34W	4031.0
5	Souчек 1	Murfin Drilling	02 01S 34W	4108.5
6	Reese F	Cities Service	22 05S 20W	3322.8
7	Holmdahl A-1	Cities Service	29 03S 31W	J-zone
8	Elvin 2	Murfin Drilling	14 03S 27W	A-zone
9	Thompson E-2	Cities Service	31 30S 33W	4150.0
SHALES				
10	Thompson E-2	Cities Service	31 30S 33W	4534.0
11	Thompson E-2	Cities Service	31 30S 33W	4746.0
12	Reidel 6	Empire Drilling	06 10S 26W	3914.8
13	Reidel 6	Empire Drilling	06 10S 26W	3937.7
14	Reidel 6	Empire Drilling	06 10S 26W	3961.0

cation analyses were performed on a Beckman Spectrametric SpectraSpan III-B Direct Current Plasma Emission Spectrometer. The results of the multiple analyses for these elements differed by less than 5 percent except for Si, analysis for which differed by approximately 7 percent.

Chloride, SO_4 , I, and Br concentrations were determined by ion chromatography at Amoco Laboratory. The Cl concentrations were also found by titrating with a standard AgNO_3 solution, following the Argentometric Method in the American Public Health Association, Standard Methods for the Examination of Water and Wastewater (1985). A Buchler Digital Chloridometer was used to check the Cl results. This titration method is based on the coulometric generation of Ag ions in situ from a Ag wire anode. These Ag ions cause the precipitation of Cl as AgCl . The endpoint is amperometrically detected at the first excess of free Ag ion. The rate of Ag ion generation is constant so the time elapsed is proportional to the amount of Cl precipitated. A few samples were also analyzed for their SO_4 content following the Turbidometric Method and using a Bauch and Lomb Spectronic 2000 Spectrophotometer (American Public Health Association, Standard Methods for the Examination of Water and Wastewater, 1985). The results of these analyses varied by an average of 4 percent.

Total alkalinity of the samples was determined by titrating the sample with a standard acid to an endpoint of 4.5 pH. This procedure is outlined in the American Public Health Association, Standard Methods for the Examination of Water and Wastewater (1985). The pH of

several water samples was also measured. Both procedures used a Cole-Parmer Model 5985-80 Digi-Sense pH Meter.

The ion concentrations reported were determined using duplicate experiments and different analytical procedures for each element whenever possible. The errors of the values for each ion overlapped indicating reproduceable results. The average relative standard deviations available for the analyzed elements are: Na, 3.3; Ca, 3.8; Mg, 3.6; Sr, 3.0; K, 1.7; Si, 7.1; and Cl, 4.0.

Duplicate oil-water samples were collected and acidified for some wells. The cation analyses for the acidified oil-field waters differed from the unacidified analyses by an average of 3 percent.

The total dissolved solids (TDS) in each water sample was found by placing 1 ml of sample in a pre-weighed container. This was then dried at 200°C and the residue weighed. The sum of the cations and anions for each water sample was also used to determine the TDS. The average percent difference between the two values for each sample was 5 percent.

ISOTOPIC DETERMINATION

Strontium was separated from the water samples using ion-exchange columns containing Dowex 50W-X8 cross-linked resin. The columns were cleaned with 2N Vycor-distilled HCl. All laboratory equipment used was soaked in a HCl solution and rinsed several times with distilled, demineralized water. A volume of water containing approximately 30 micrograms of Sr was pipetted into a teflon beaker and evaporated to dryness. The salt was then redissolved in 2ml of 2N HCl

and put into the column. Each column was eluted with 55ml of 2N HCl. Strontium chloride was then collected in 2ml fractions and evaporated to dryness. The samples containing mostly Sr were transferred into a microbeaker and heated to remove any organic residue.

The exchangeable Sr from two of the shale samples was separated in order to determine its isotopic ratios. Approximately 1/4 g of the <0.2 micron fraction of two shale samples was soaked in 15ml of 0.2N HCl for 1 hour. The sample was then filtered and the Sr separated using the ion-exchange columns as discussed previously. Carbonate and vug-fill material from the cores was also analyzed for its Ca, Mg and Sr content. Samples were removed, weighed, and dissolved in 0.1N HCl. The solution was then filtered and diluted to a known volume. The appropriate amount of sample was placed in the ion-exchange columns and Sr separated.

The Sr isotopic ratios of the samples were determined by mass spectrometry at CONOCO Laboratory. Replicate analysis of Eimer and Amend standard Sr gave a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70807 ± 0.00002 at the 95 percent confidence level. The oxygen and hydrogen isotopic data for the water samples were determined at the Geochron Laboratories Division of Krueger Enterprises, Inc. in Cambridge, Massachusetts.

X-RAY DIFFRACTION

Five shale samples were collected from cores of Lansing-Kansas City strata stored at the Kansas Geological Survey in Lawrence, Kansas (Table 2). The samples were soaked in distilled, demineralized water to remove surface contamination. After the water was decanted off, a

mortar and pestle were used to crush the samples. Each sample was then placed in a blender to disaggregate it further. The resulting slurry was suspended in distilled, demineralized water. Size fractions of 2.0 - 0.2 and <0.2 microns were separated using a centrifuge. Oriented slides were made by placing the clay slurry on a clean glass slide and allowing it to air dry. The slides were subsequently treated with ethylene glycol and hydrazine vapors and were also heated to 450°C for 1 hour and heated to 600°C for 1 hour. After each procedure the samples were x-rayed using a Norelco X-ray Diffractometer with a Ni filter and a Cu K α source.

PETROGRAPHY

Acetate peels of the carbonate rocks were prepared for mineralogic and textural identification. The surface of each sample was smoothed using 600 grit. Each sample was placed in a 1.5 percent HCl solution for 20 seconds to etch the surface and then placed in a solution of potassium ferricyanide and Alizarian Red S for 45 seconds. This solution stains non-ferroan calcite red, ferroan calcite blue, and dolomite white. The etched and stained surface was flooded with acetone and immediately covered with acetate. This was allowed to air dry.

The relief on the grains due to differential etching by the acid and the stain are preserved on the acetate peel. The peels were examined through a petrographic microscope. Thin sections of one core were also prepared and examined under a petrographic microscope.

GEOLOGY OF THE STUDY AREA

REGIONAL GEOLOGY

Merriam (1963) provides a basic discussion of the geologic history of Kansas from which the following material is taken. Kansas is located on a platform-like extension of the Canadian Shield, the rocks of which form the basement complex in Kansas. Deformation has subsequently altered the shape and configuration of pre-Mississippian structures making them difficult to recognize. Many of the structures that began to develop during late Mississippian or early Pennsylvanian time define the structural framework observed in Paleozoic strata. The early Pennsylvanian structures have not been materially altered by post-Paleozoic movements.

The study area is located on the western flanks of the Central Kansas Uplift and Pratt Anticline, on the Cambridge Arch, and within the Hugoton Embayment of the Anadarko Basin (Fig. 3). The Central Kansas Uplift is the largest positive structural feature in Kansas. Trending northwest, it separates the Hugoton Embayment on the west from the Salina and Sedgwick Basins on the east (Fig. 3). The Central Kansas Uplift was structurally active during early Pennsylvanian time. On the flanks of the structure, pre-Pennsylvanian strata are upturned, truncated, and overlain by Pennsylvanian beds. On the crest of the uplift, Precambrian rocks are overlain by Pennsylvanian rocks (Fig. 4). Permian beds above the structure are similar to those found in adjacent areas. Cretaceous, Tertiary, and Quaternary formations mask

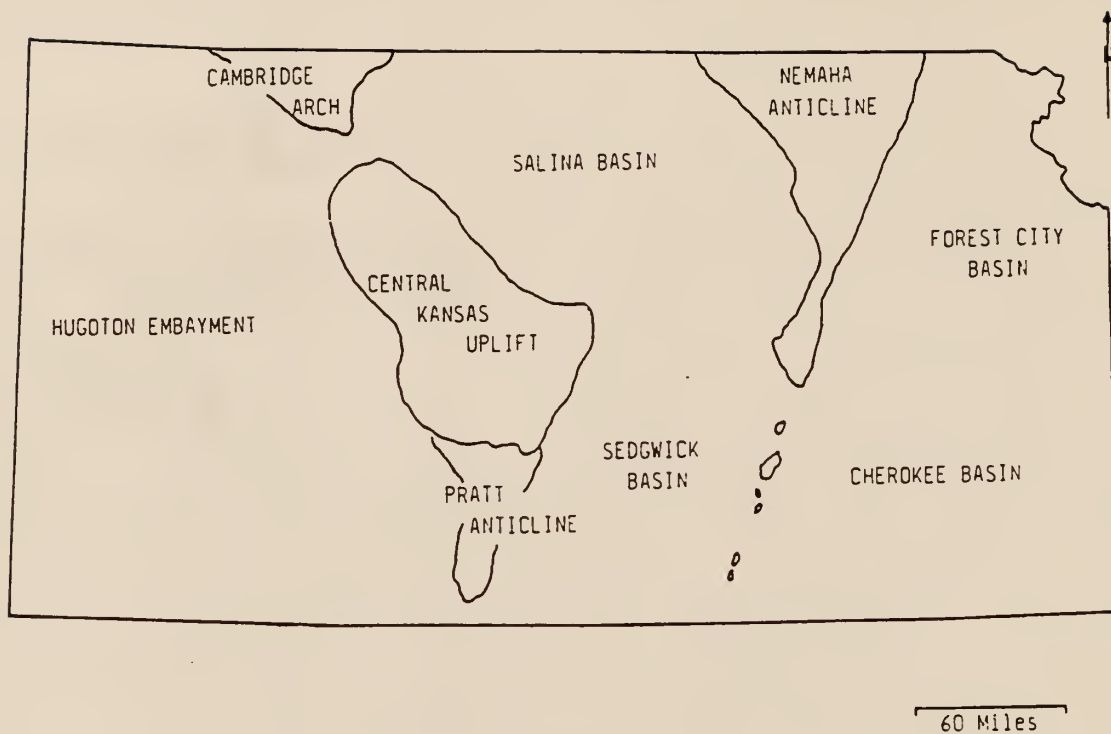


Figure 3. Major structural features in Kansas (after Merriam, 1963).

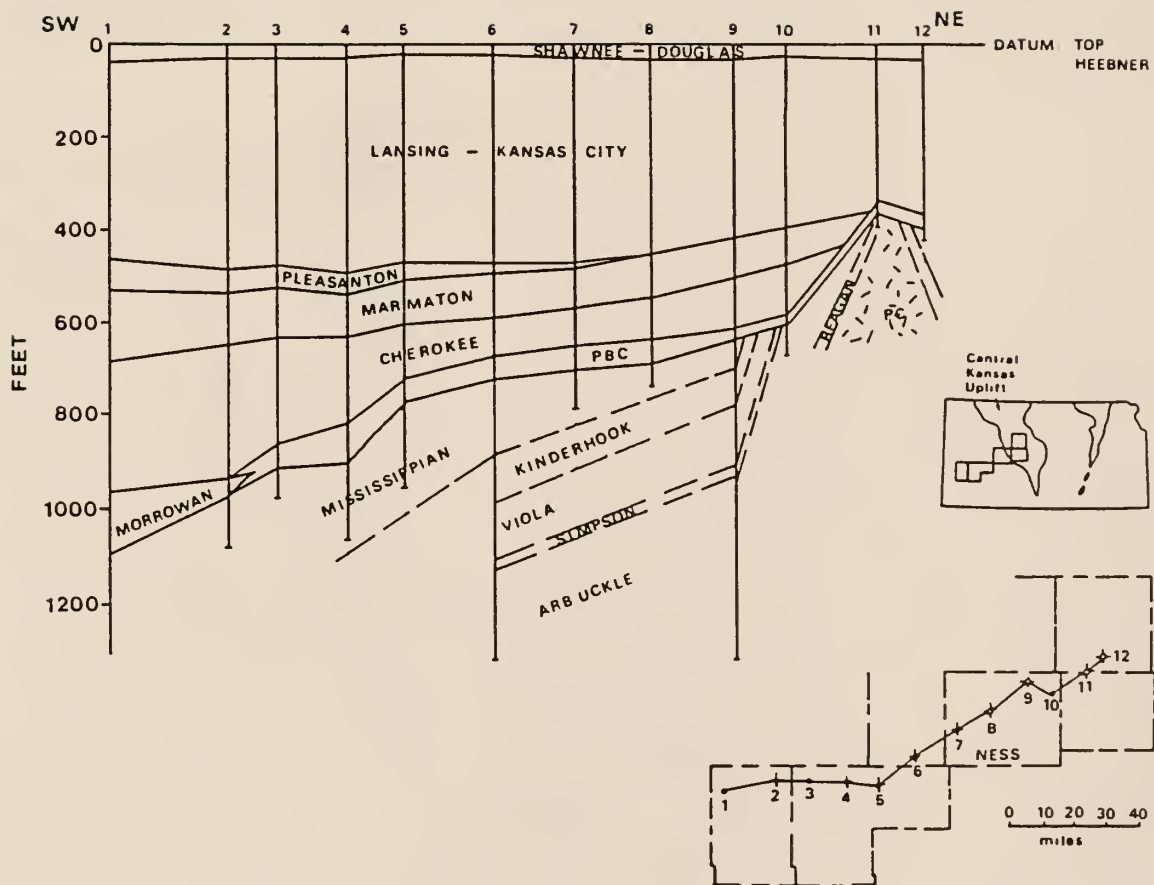


Figure 4. Generalized geologic cross section through the study area (after Merriam, 1963).

the underlying structure, movement of which ceased prior to Cenozoic time.

The Pratt Anticline, located on the southern end of the Central Kansas Uplift separates the Hugoton Embayment on the west from the Sedgwick Basin to the east. The deformation of the Pratt Anticline, a southward-plunging anticline, occurred during early Paleozoic and also early Pennsylvanian. Mississippian rocks are absent over the crest of the anticline and Pennsylvanian rocks overlies those of Ordovician age.

The southern end of the Cambridge Arch extends into northwestern Kansas from Nebraska (Fig. 3). This northwest-trending anticlinal feature is separated from the Central Kansas Uplift to the southeast by a structural saddle. Structural movement occurred during pre-Mississippian, early Pennsylvanian, and Mesozoic times. Precambrian crystalline rocks are overlain by Pennsylvanian strata on the crest of the arch, and on the flanks older Paleozoic rocks are deformed similar to those on the flanks of the Central Kansas Uplift.

The Hugoton Embayment, occupying about the western one-third of Kansas, is a large shelf-like extension of the Anadarko Basin found in Oklahoma and Texas (Fig. 5). The boundaries of the Hugoton Embayment are the Central Kansas Uplift, Cambridge Arch, and Pratt Anticline on the east and the Las Animas Arch of eastern Colorado on the west. Sediments within the structure thicken toward the axis and southward in the direction of structural plunge. Facies changes within the Paleozoic sedimentary units, occur toward the Anadarko Basin to the south and the Rocky Mountains to the west. Precambrian rocks within the Hugoton Embayment are overlain by as much as 9,500 feet of younger

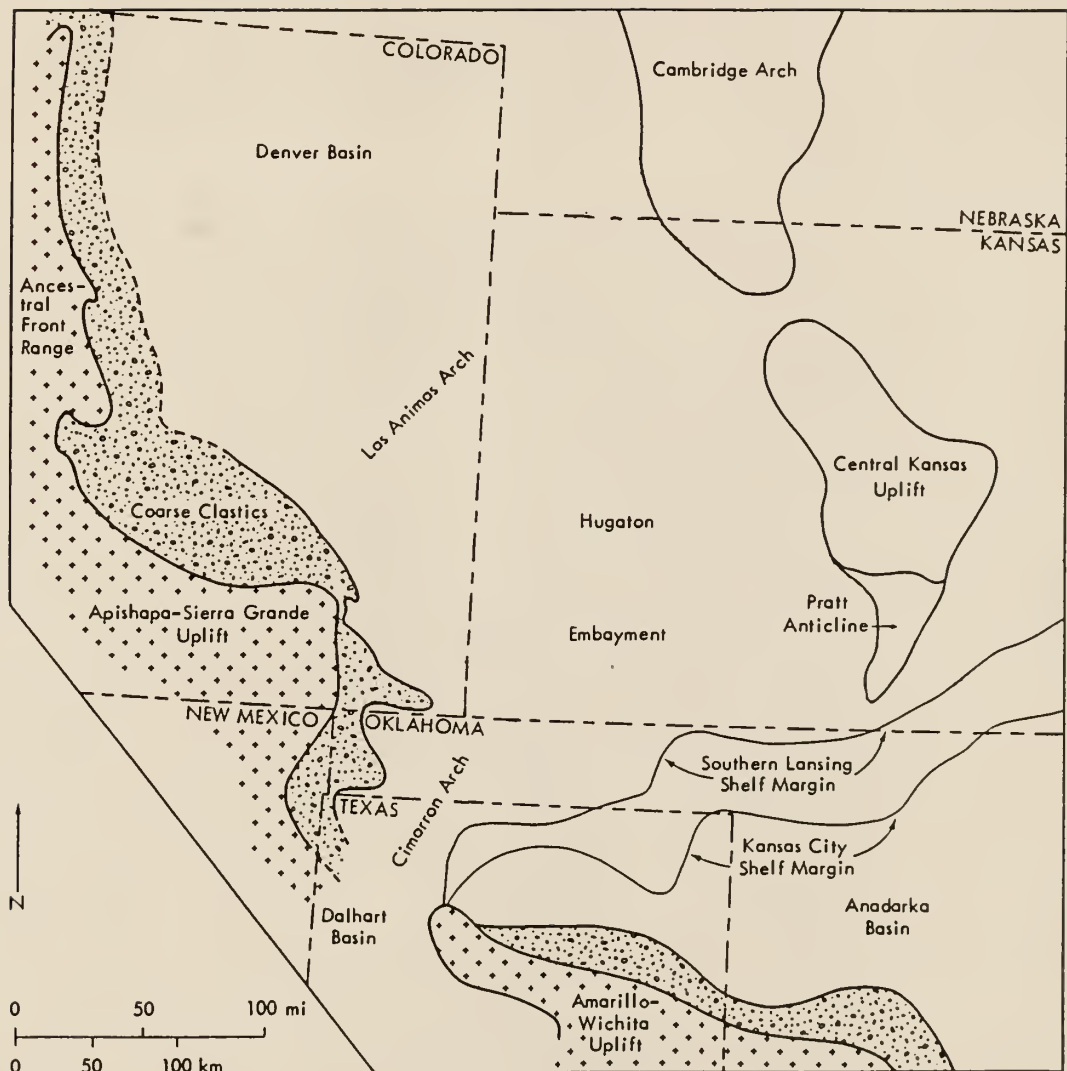


Figure 5. Missourian (Late Pennsylvanian) paleogeographic map of western Kansas and adjacent areas (modified from Watney, 1980).

material. Structural development concluded prior to the Mesozoic allowing Cretaceous and younger beds to mask the underlying structure.

LANSING-KANSAS CITY STRATIGRAPHY OF THE STUDY AREA

The Upper Pennsylvanian series in Kansas is composed of nearly 1,800 feet of limestone, shale, and sandstone. This sequence is divided into two stages, the Missourian below and the Virgilian above (Fig. 6). The Missourian stage makes up about one third of the section and averages 650 feet thick (Zeller, 1968). The Lansing-Kansas City Groups make up the upper and middle parts of the Missourian stage. According to Zeller (1968) the Kansas City Group averages 340 feet thick and is divided into six limestone formations separated by shale formations. The Lansing Group, having an average thickness of 85 feet, is divided into one shale and two limestone formations (Fig. 7). In western Kansas, these groups are present in the subsurface, but they are usually not separated.

The rocks of the Lansing-Kansas City Groups in western Kansas thicken from about 300 feet in the north to 550 feet in the south (Watney, 1980). Cross-sections of the Lansing-Kansas City Groups were prepared using subsurface data (Figs. 8 and 9). These show an increase in the thickness of the rocks westward and southward.

Heckel (1977, 1984, 1985, and 1986) and Watney (1980 and 1985) describe the rocks of the Lansing-Kansas City Groups as cyclic sequences of alternating limestones and shales. Each cycle consists of four depositional units: a basal transgressive limestone, overlain

SYSTEM	SERIES	STAGE	GROUP
PENNSYLVANIAN	UPPER	VIRGILIAN	Wabaunsee
			Shawnee
			Douglas
		MISSOURIAN	Lansing
			Kansas City
			Pleasanton
	MIDDLE	DES MOINESIAN	Marmaton
			Cherokee
		----- ATOKAN	
	LOWER	MORROWAN	

Figure 6. Generalized stratigraphic column of Pennsylvanian rocks in western Kansas (modified from Zeller, 1968).

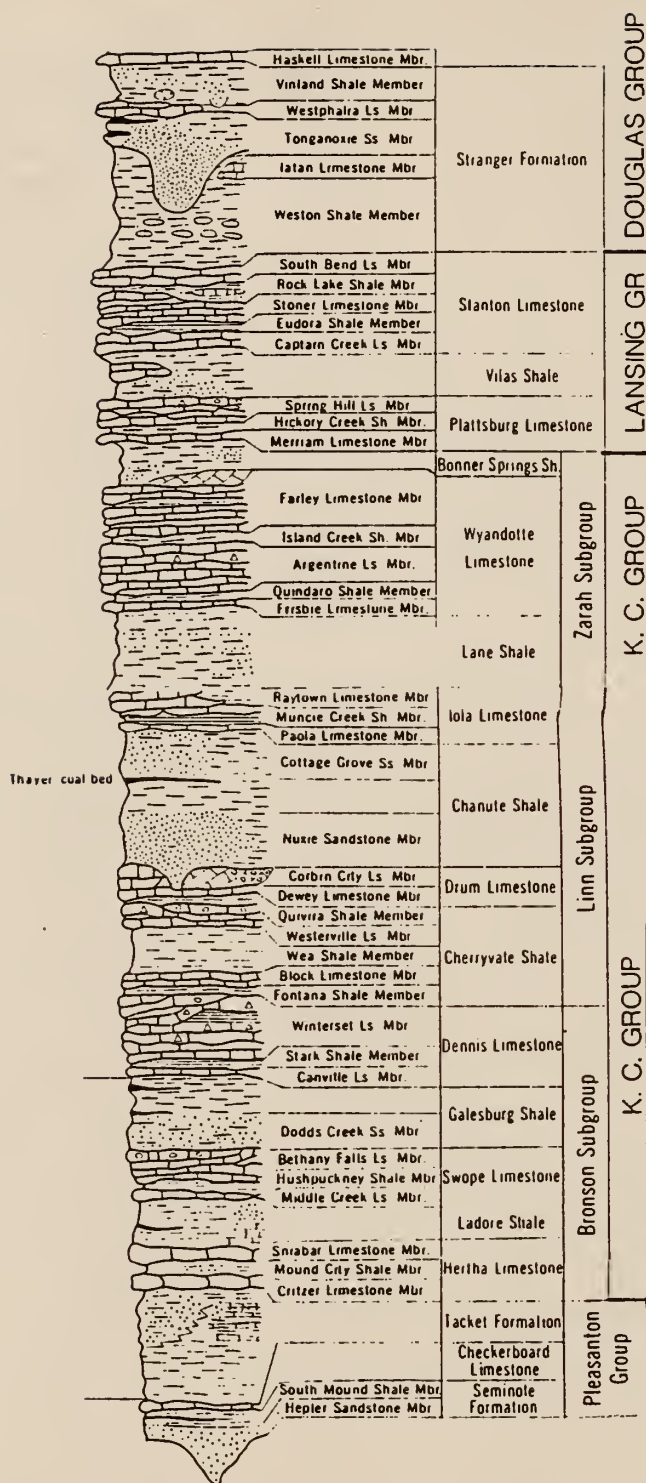


Figure 7. Formal member and formation nomenclature of the Lansing-Kansas City Groups in Kansas (modified from Watney, 1985).

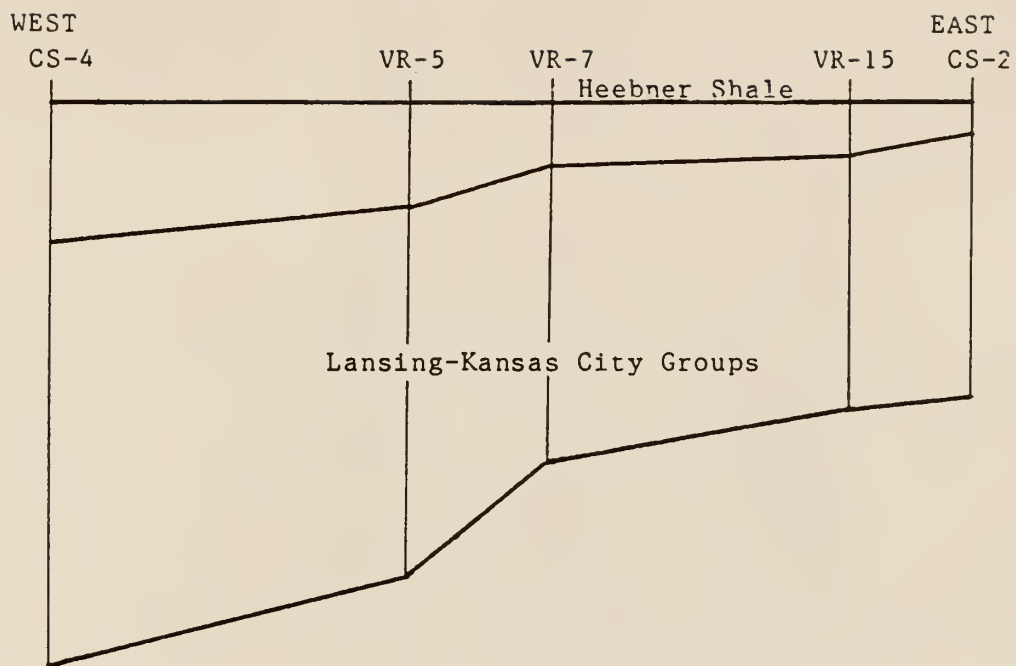


Figure 8. East-west cross section of the Lansing-Kansas City Groups through the study area.

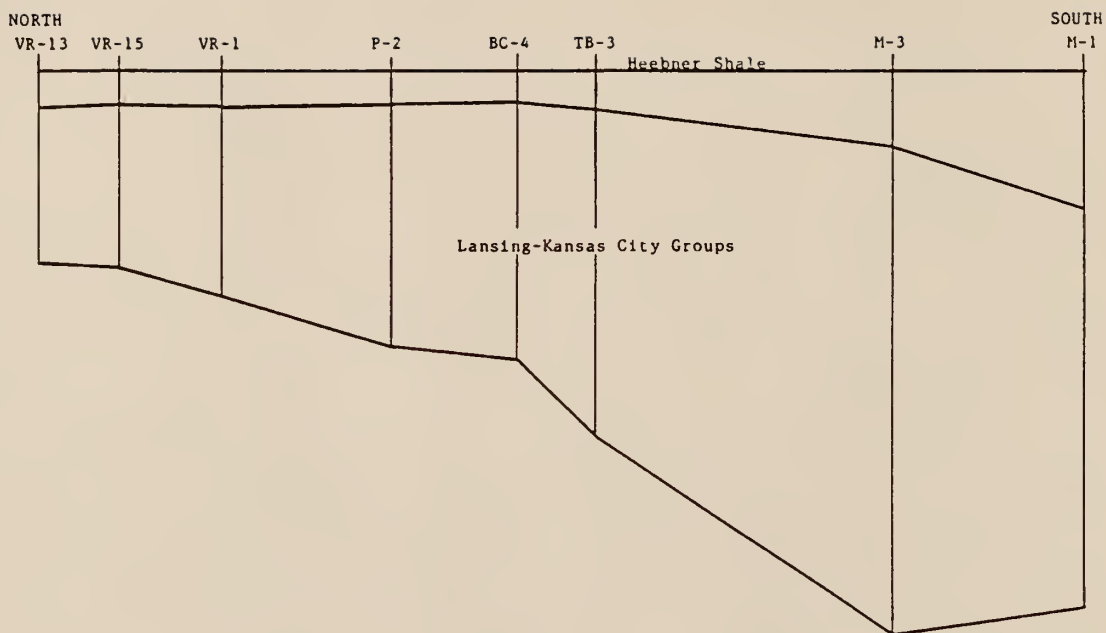


Figure 9. North-south cross section of the Lansing-Kansas City Groups through the study area.

by an offshore marine shale, a regressive limestone, and capped by a regressive nearshore shale (Fig. 10). Heckel (1977 and 1985) provided basic descriptions of the units which are reviewed below.

Basal Transgressive Limestone

The basal transgressive limestone was deposited in deepening water, and typically consists of a thin marine skeletal calcilutite deposited below the effective wave base but may locally include calcarenites at the base. These limestones are usually dark, dense, nonpelleted, and lack evidence of early marine cementation or meteoric leaching and cementation. This is due to their remaining in a deep water environment until burial by the successive layer of the cyclothem which acted as an impermeable membrane to meteoric diagenesis. This allowed the limestone to undergo slow compaction before cementation.

Offshore Marine Shale

The offshore marine or core shale was formed during the period of maximum transgression. This is typically a thin non-sandy gray to black phosphatic shale deposited at a very low rate of sediment influx. The deepening water produced a thermocline over most or all of the lower shelf areas of the midcontinent causing bottom-oxygen to be reduced or eliminated. This allowed only low-oxygen benthic invertebrates to be present within the gray dysaerobic facies deposited in the shallower areas. In the deeper areas black anoxic facies rich in organic matter, heavy metals, and phosphate were deposited containing only pelagic fossil remains.

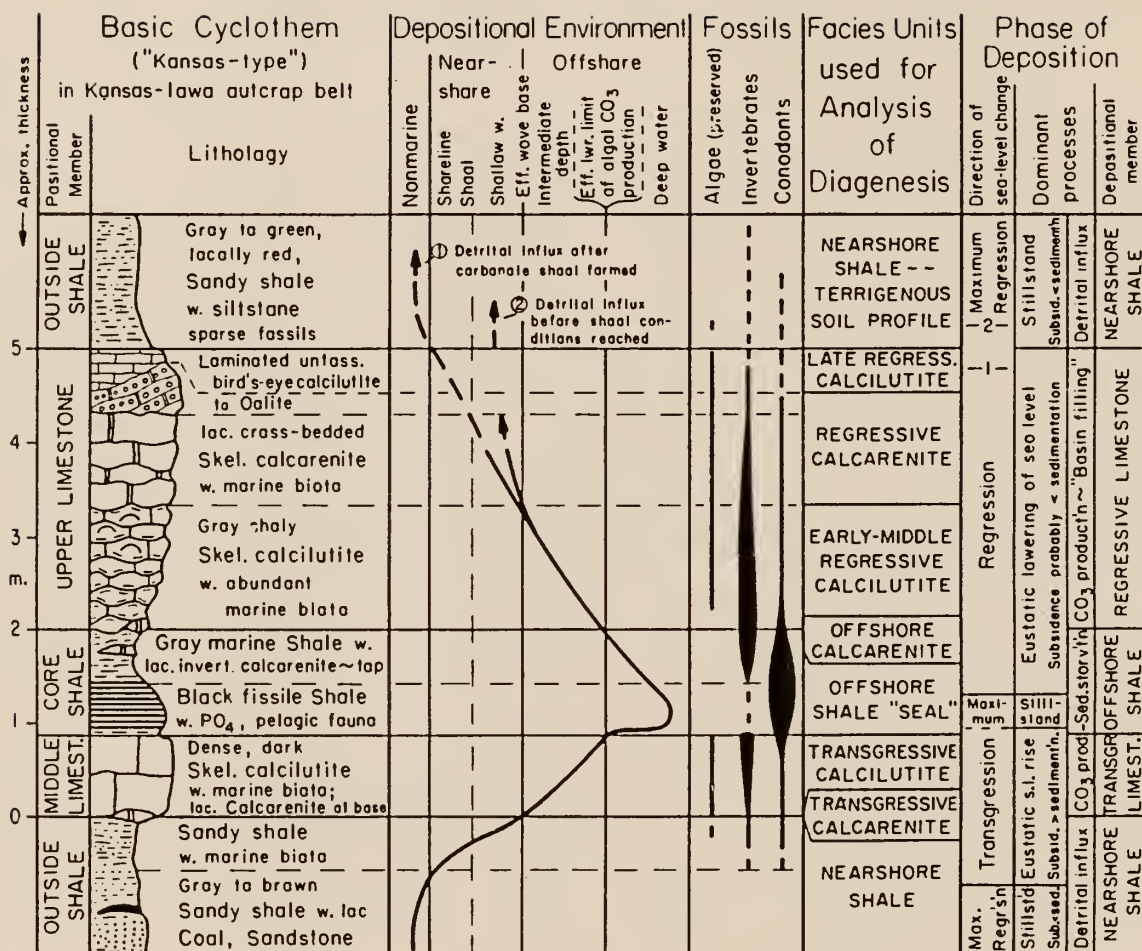


Figure 10. Basic sequence of Midcontinent Pennsylvanian "Kansas cyclothem" (from Heckel, 1983).

In the gray facies, aragonite fossils were dissolved and are now preserved as siderite, pyrite, or phosphorite. Calcite fossils were locally corroded and ammonoids are preserved locally in early diagenetic carbonate nodules within the black facies.

In both the gray and black facies non-skeletal phosphorite was deposited as granules, laminae, and nodules. These were due to upwelling associated with the thermocline.

Upper Regressive Limestone

The upper regressive limestone was deposited in shallowing water. These consist mainly of a thick marine skeletal calcilutite that was deposited below the wave base. This grades upward into a skeletal calcarenite with abraided grains, cross-bedding, and algae, all evidence for shallow water transport.

A different calcarenite is associated with the offshore shale in some cyclothems. This calcarenite was deposited below the effective wave base and probably below the photic base. As in the transgressive limestones, these calcarenites exhibit overcompaction due to deep burial prior to cementation.

Some regressive limestones contain cross-bedded oolites which formed in deeper agitated supersaturated waters. Others display birdseye-bearing lagoonal to peritidal carbonates at the top representing strandline passage. These shoreline facies may not be present, but the passage of the strandline is recorded by subaerial exposure surfaces within the upper parts or on top of the regressive limestones. These surfaces, formed by weathering in the presence of

meteoric water, often appear mottled and rusty due to overlying shale and iron oxide being carried down into the void spaces in the limestone. Caliche crusts are formed where the meteoric water becomes supersaturated on the limestone surface.

Outside Shale

The outside, nearshore shale includes a variety of terrestrial and nearshore marine sediments deposited on the shelf during a period of sea level minimum. Clastic influx was greatly increased at this time. These units include thick, sparsely fossiliferous prodeltaic shales which in places may grade upward into delta-front and delta-plain sandstones and coals. Thinner, blocky textured mudstones containing irregular carbonate nodules are also present which suggests they originated as paleosols.

The sequence composed of these four basic units (basal transgressive limestone, offshore marine shale, upper regressive limestone, and outside shale) is considered by Heckel (1977, 1983, 1984, 1985, and 1986) and Watney (1980 and 1985) to represent the basic transgressive-regressive Kansas cyclothem that resulted from a major rise and fall of sea level over the northern Midcontinent shelf. Busch et al. (1985) believe that the cyclothem approach is too general and ignores many smaller-scale transgressive-regressive sequences within the four basic units.

Classification Of Zones

Informal classification systems have been applied to the rocks of the Lansing-Kansas City Groups. Zones, generally based on cyclothems, were assigned using electric logs. Having located the top of the Lansing Group, each major limestone identified was assigned to the subsequent zone.

Figure 11 shows three classification systems that have been applied to the Lansing-Kansas City Groups, two of which are used in Kansas. The same letter designation assigned by the two different classification systems that use letters(1 and 2; Fig. 11) would most likely refer to different stratigraphic intervals. This could cause error when analyzing data identified by production zone. However, within Kansas the Nebraska system (1; Fig. 11) is not used and with very few exceptions, the electric logs substantiate the reported zone of production (James Anderson, personal communication, 1987).

DIAGENESIS OF LANSING-KANSAS CITY STRATA

The transgressive and regressive limestones within each cyclothem were deposited in similar depositional environments within the marine phreatic zone though in reverse order. Differences between the transgressive and regressive limestones have been observed and attributed to different diagenetic histories. Heckel (1983) derived a diagenetic model for these limestones which Prather (1984) and Watney (1980 and 1984) have applied to rocks of the Lansing-Kansas City Groups.

Theodore Gore Co. Wertz #1
SE NW Sec. 6, T.2N., R.32W.
Hitchcock Co., Nebraska
Meeker Canal Field
Discovery Well

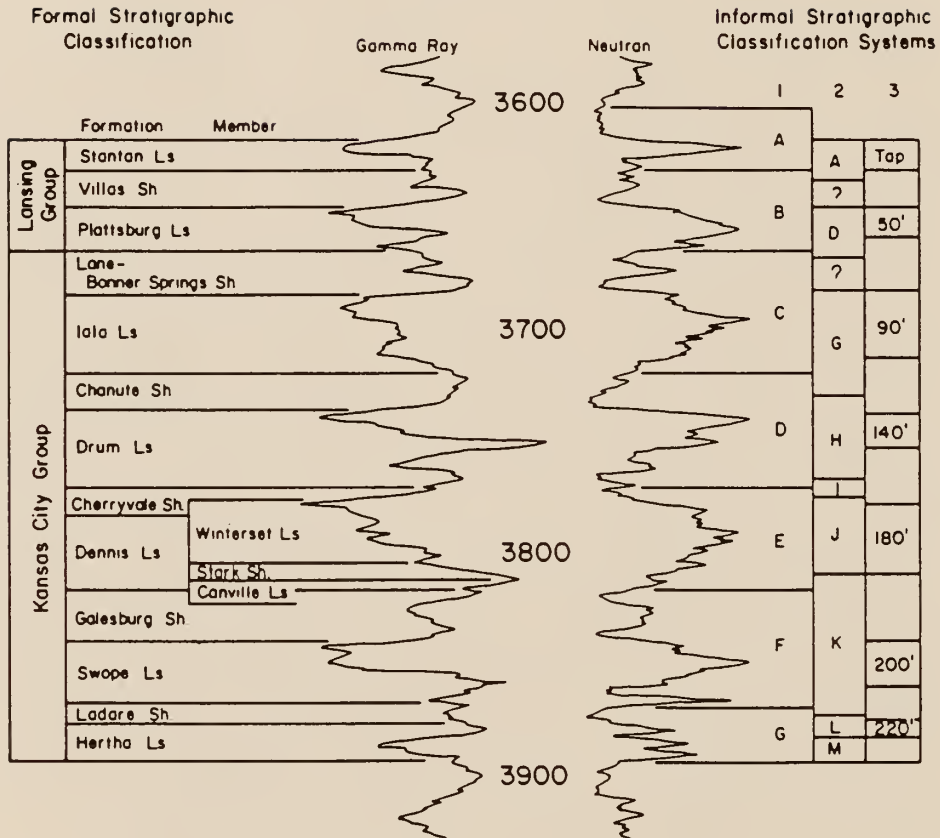


Figure 11. Stratigraphic classification schemes for the Lansing-Kansas City Groups: 1) commonly used in Nebraska, 2) commonly used in northwest Kansas, 3) based on depth below top of Lansing, used some in central Kansas (modified from Dubois, 1985).

According to Heckel (1983 and 1984), at the end of each cycle of deposition, if the sea withdrew sufficiently, meteoric water could infiltrate into the regressive limestone. The upper portions of this limestone would progressively be subjected to the phreatic mixing zone with brackish salinities, the saturated meteoric water zone where blocky calcite cement readily precipitates, and the unsaturated meteoric zone where unstable grains are leached. The limestone would move back through these zones in reverse order as the subsequent transgression takes place. Evidence for this process includes widespread early fresh-water cementation, leached ooids, mollusks, and algae, collapse of unsupported material, and further cementation in oxygenated water preserving the brecciated algal-mound or leached oomoldic fabric. Ferroan dolomite deposited under low-oxygen conditions occurs in the remaining restricted zones of permeability.

Heckel (1983 and 1984) believes the transgressive limestones were protected from fresh-water infiltration by the offshore shale which acts as an impermeable membrane deposited between the transgressive limestone and the regressive limestone above. The transgressive limestone was buried completely within the marine phreatic environment of deposition. These limestones, lacking early cements, underwent slow grain-to-grain compaction under decreasing oxygenated conditions. Unstable grains were neomorphosed. The transgressive limestones exhibit overpacking of grains in welded to stylolitic grain contacts, and contain crushed shells. Also present are neomorphosed ooids, mollusks, and algae. Low-oxygen, late-stage ferroan calcite and

dolomite cements are present in the intergranular pore spaces which have been greatly reduced by compaction.

RESULTS

CHEMICAL DATA OF WATERS

Sulin's classification of oil-field waters has been reviewed by Collins (1975). According to this scheme, all of the oil-field waters sampled are Chloride-Calcium Type except for BC-2, BC-9, CS-1, and CS-4 which are Chloride-Magnesium Type. The oil-field waters analyzed were all more concentrated than sea water with TDS values between 40,900 and 217,000 mg/l (Table 3). The lowest TDS is in sample CS-4 located in the northwest corner of the study area. The southern-most sample, M-1, has the highest TDS value.

The pH of several randomly scattered samples was measured and found to be between 6.5 and 7.8 (Table 3). The highest pH was found in sample CS-4 located in the northwest corner and the low pH's were found in samples in the southern and eastern portions of the study area. These values were determined in the laboratory sometime after collection and therefore they should be used with caution.

Analyses of oil-field waters from the Lansing-Kansas City Groups are summarized in tables 3 and 4. Tables 5 and 6 summarize the concentrations of cations and anions in miliequivalents per liter (meq/l) for each water sample. Table 7 contains the ranges of values for the analyzed chemical constituents. Sodium concentrations varied between 17,000 and 51,000 mg/l. Calcium values generally ranged from 960 to 5,000 mg/l except for samples CS-4 located in the northwest

Table 3. Major cation and TDS analyses of Lansing-Kansas City oil-field waters, western Kansas.
(concentrations expressed in mg/l)

Sample	Ca	Mg	Na	Sr	K	Rb	Li	Si	TDS	pH
BC-1	2,500	650	31,000	79	370	0.50	7.2	8.40	107,000	---
BC-3	1,600	480	42,000	56	150	0.37	4.4	7.30	122,000	---
BC-4	1,900	480	40,000	52	410	0.49	4.5	8.50	122,000	---
BC-6	4,300	1,600	23,000	200	150	0.24	8.8	6.90	92,700	6.5
BC-8	5,000	1,900	40,000	1,100	300	0.39	6.1	6.50	133,000	---
BC-10	2,000	500	36,000	61	370	0.24	5.0	9.10	109,000	---
BC-11	1,600	470	34,000	51	380	0.51	5.1	8.90	103,000	---
BC-12	1,200	410	33,000	62	800	0.50	6.0	9.20	96,000	7.3
BC-13	1,300	360	41,000	44	380	0.59	6.9	8.40	115,000	---
BC-14	1,900	490	37,000	58	380	0.47	4.9	8.40	106,000	---
BC-15	1,000	320	17,000	28	430	0.38	5.5	11.00	56,600	7.4
BC-16	1,400	430	24,000	36	300	----	---	----	83,300	---
CS-2	2,000	870	21,000	120	210	0.21	4.3	5.70	116,000	---
M-1	11,100	2,500	33,000	1,400	430	0.54	8.2	5.40	217,000	6.7
M-3	8,900	2,700	60,000	850	650	0.62	3.4	4.30	189,000	---
P-4	1,300	330	35,000	38	<30	0.42	4.1	5.20	109,000	---
TB-1	1,400	420	28,000	42	<30	0.42	5.7	9.70	93,800	---
TB-5	2,300	660	46,000	63	600	0.48	4.7	8.80	153,000	---
TB-6	2,400	530	34,000	69	310	0.44	5.1	10.00	106,000	---
VR-2	2,400	670	35,000	84	280	0.32	4.8	8.50	110,000	---
VR-5	2,400	500	23,000	69	140	0.20	4.8	11.00	94,300	---
VR-6	3,100	640	28,000	76	150	0.18	4.7	9.60	115,900	---
VR-7	1,900	630	54,000	47	200	0.18	5.7	6.40	185,000	---
VR-13	2,500	980	51,000	62	160	0.10	5.4	4.70	175,000	7.3
VR-14	2,500	730	51,000	56	150	0.15	4.7	4.40	165,000	---
BC-2*	1,700	430	49,000	54	500	0.36	6.6	8.80	147,000	---
BC-9*	960	380	33,000	52	240	0.18	4.9	9.40	86,200	---
CS-1*	3,800	1,700	35,000	250	130	0.14	3.0	7.50	81,500	---
CS-4*	600	120	17,000	21	150	0.17	1.9	14.00	40,900	7.8

* - These waters are Cl-Mg Type, the remainder are Cl-Ca type

Table 4. Anion analyses of Lansing-Kansas City oil-field waters,
western Kansas.
(concentrations expressed in mg/l)

<u>Sample</u>	<u>Cl</u>	<u>SO₄</u>	<u>HCO₃</u>	<u>Br</u>	<u>I</u>
BC-1	56,600	1,500	150	51	21.0
BC-3	67,000	5,670	160	40	6.0
BC-4	66,900	5,520	180	75	4.0
BC-6	54,500	85	310	190	4.0
BC-8	75,700	100	330	256	5.0
BC-10	61,800	3,150	220	66	2.0
BC-11	58,000	3,770	200	63	2.0
BC-12	54,300	2,090	300	69	1.2
BC-13	68,200	3,240	180	100	1.0
BC-14	58,900	700	80	66	1.5
BC-15	27,400	5,020	280	72	1.2
BC-16	41,500	4,360	240	55	1.6
CS-2	66,400	31	290	56	1.5
M-1	125,400	140	90	450	5.0
M-3	111,100	140	110	33	5.0
P-4	57,800	4,640	110	178	5.0
TB-1	50,600	3,320	420	60	1.6
TB-5	87,400	2,120	150	111	2.0
TB-6	56,100	2,740	320	83	1.7
VR-2	58,600	3,030	240	105	1.0
VR-5	46,000	2,340	430	50	1.0
VR-6	58,400	2,470	270	47	1.0
VR-7	100,200	3,540	160	19	0.5
VR-13	90,100	3,800	130	50	1.0
VR-14	88,900	3,320	140	46	1.0
BC-2*	71,900	930	180	54	5.0
BC-9*	51,300	2,910	380	67	2.0
CS-1*	43,000	16	110	88	1.2
CS-4*	22,600	5,000	480	78	2.4

* - These waters are Cl-Mg Type, the remainder are Cl-Ca type

Table 5. Major cation analyses of Lansing-Kansas City oil-field waters,
western Kansas.
(concentrations expressed in meq/l)

<u>Sample</u>	<u>Ca</u>	<u>Mg</u>	<u>Na</u>	<u>Sr</u>	<u>K</u>	<u>Li</u>	<u>Si</u>
BC-1	124.8	53.5	1348	1.8	9.5	1.0	1.2
BC-3	79.8	39.5	1827	1.2	3.8	0.6	1.0
BC-4	94.8	39.5	1740	1.2	10.5	0.6	1.2
BC-6	214.6	131.6	1000	4.6	3.8	1.0	1.0
BC-8	249.6	156.3	1740	25.1	7.7	0.9	0.9
BC-10	99.8	41.1	1566	1.4	9.5	0.7	1.3
BC-11	79.8	38.7	1479	1.2	9.7	0.7	1.3
BC-12	59.8	33.7	1435	1.4	20.5	0.9	1.3
BC-13	64.8	29.6	1783	1.0	9.7	1.0	1.2
BC-14	94.8	40.3	1609	1.3	9.7	0.7	1.2
BC-15	50.0	26.3	739	0.6	11.0	0.8	1.6
BC-16	69.9	35.4	1044	0.8	7.7	---	---
CS-2	99.8	71.6	913	2.7	5.4	0.6	0.8
M-1	553.8	205.7	1435	32.0	11.0	1.2	0.8
M-3	444.2	222.1	2610	19.4	16.6	0.5	0.6
P-4	64.8	27.1	1522	0.9	---	0.6	0.7
TB-1	69.8	34.6	1218	1.0	---	0.8	1.4
TB-5	114.8	54.3	2001	1.4	15.3	0.7	1.3
TB-6	119.8	43.6	1479	1.6	7.9	0.7	1.4
VR-2	119.8	55.1	1522	1.9	7.2	0.6	1.2
VR-5	119.8	41.1	1000	1.6	3.6	0.7	1.6
VR-6	154.4	52.6	1218	1.7	3.8	0.7	1.4
VR-7	94.8	51.8	2349	1.1	5.1	0.8	0.9
VR-13	124.8	80.6	2218	1.4	4.1	0.8	0.7
VR-14	124.8	60.1	2218	1.3	3.8	0.7	0.6
BC-2*	84.8	35.4	2131	1.2	12.8	1.0	1.3
BC-9*	48.0	31.3	1435	1.2	6.1	1.4	1.3
CS-1*	189.9	139.8	1522	5.7	3.3	0.4	1.1
CS-4*	30.0	9.9	739	0.5	3.8	0.3	2.0

* - These waters are Cl-Mg Type, the remainder are Cl-Ca type

Table 6. Anion analyses of Lansing-Kansas City oil-field waters, western Kansas.
(concentrations expressed in meq/l)

<u>Sample</u>	<u>Cl</u>	<u>SO₄</u>	<u>HCO₃</u>	<u>Br</u>
BC-1	1,596	31.2	2.5	0.6
BC-3	1,890	118.0	2.6	0.5
BC-4	1,887	114.9	2.9	0.9
BC-6	1,537	1.8	5.1	2.4
BC-8	2,135	2.1	5.4	3.2
BC-10	1,743	65.6	3.6	0.8
BC-11	1,636	78.5	3.3	0.8
BC-12	1,532	43.5	4.9	0.9
BC-13	1,924	67.5	2.9	1.3
BC-14	1,661	14.6	1.3	0.8
BC-15	772	104.5	4.6	0.9
BC-16	1,171	90.8	3.9	0.7
CS-2	1,873	0.6	4.8	0.7
M-1	3,537	2.9	1.5	5.6
M-3	3,134	2.9	1.8	0.4
P-4	1,630	96.6	1.8	2.2
TB-1	1,427	69.1	6.9	0.8
TB-5	2,465	44.1	2.5	1.4
TB-6	1,582	57.0	5.2	1.0
VR-2	1,653	63.1	3.9	1.3
VR-5	1,297	48.7	7.0	0.6
VR-6	1,647	51.4	4.4	0.6
VR-7	2,826	73.7	2.6	0.2
VR-13	2,541	79.1	2.1	0.6
VR-14	2,508	69.1	2.3	0.6
BC-2*	2,028	19.4	2.9	0.7
BC-9*	1,447	60.6	6.2	0.8
CS-1*	1,213	0.3	1.8	1.1
CS-4*	637	104.1	7.9	1.0

* - These waters are Cl-Mg Type, the remainder are Cl-Ca type

Table 7. Ranges of chemical and isotopic values for the Lansing-Kansas City waters.

<u>Chemical Constituent</u>	<u>Minimum</u>	<u>Maximum</u>
CATIONS (mg/l)		
Na	17,000	51,000
Ca	600	11,100
Sr	21	850
Mg	120	2,600
K	130	<3
Si	4.3	14.0
Li	0.7	8.8
RB	0.1	0.6
ANIONS (mg/l)		
Cl	22,600	125,400
SO ₄	16	5,670
HCO ₃	80	480
Br	19	450
I	0.5	21.0
ISOTOPES		
δD	-64	-16
δ ¹⁸ O	-7.5	+10.3
⁸⁷ Sr/ ⁸⁶ Sr	0.70882	0.71506

with a concentration of 600 mg/l and samples M-1 and M-3 located in the south with values of 11,100 and 8,900 mg/l, respectively. Strontium values ranged mostly from 21 to 120 mg/l. Some samples had high Sr values including samples BC-6 (200 mg/l), BC-8 (1,100 mg/l), and CS-1 (250 mg/l) in the east and M-1 (1,400 mg/l) and M-3 (850 mg/l) in the south. Magnesium values were between 320 and 980 mg/l over much of the study area. A low value of 120 mg/l was found in sample CS-4. High values between 1,700 mg/l and 2,600 mg/l were found in samples from the eastern and southern edges of the study area. Concentrations of K were between 130 and 800 mg/l except for two samples (TB-1 and P-4) in the center of the study area that were below 3.0 mg/l. Silicon, Li, and Rb were present in small amounts with values between 4.3 and 14.0 mg/l, 0.67 and 8.8 mg/l, and 0.14 and 0.62 mg/l respectively. Chloride was the major anion present in the waters with values between 22,600 and 125,400 mg/l. Sulfate values mostly ranged from 930 to 5670 mg/l, but low values were found for BC-6 (85 mg/l), BC-8 (100 mg/l), CS-1 (16 mg/l), and CS-2 (31 mg/l) in the east and M-1 (140 mg/l) and M-3 (140 mg/l) in the southern portion of the study area. Bicarbonate, values were between 80 and 480 mg/l. As they were determined in the laboratory some time after sample collection, the values must be used with caution. The concentration of Br varied between 19 and 190 mg/l, except for samples BC-8 in the east and M-1 in the south with values of 256 and 450 mg/l, respectively. Iodide ranged from 0.5 to 6.0 mg/l, with one high value of 21.0 mg/l in sample BC-1.

The concentration of each chemical constituent in the oil-field waters has been compared to that in evaporating sea water at the same Cl level (Collins, 1974). This comparison with sea water reveals relative enrichment and depletion of each ion in the oil-field waters.

Many of the oil-field waters have Na values that plot very close to the Na/Cl ratio of halite and are close to the sea water evaporation curve (Fig. 12). Samples CS-1 and CS-4 are slightly enriched in Na, whereas, BC-6, CS-2, M-1, M-3 and VR-6 are slightly depleted in Na. Different stratigraphic units underlie the Lansing-Kansas City Groups within the study area. No discernable effect, of the different underlying units, can be found on the Na/Cl ratio of the waters (Fig. 12). Neither can any production zone control be found on the Na/Cl ratio of the oil-field waters (Fig. 13). The spatial distribution of concentration indicates that Na is generally highest through the central portion of the study area (Fig. 14).

A few of the oil-field waters' Ca/Cl ratios plot close to the sea water evaporation curve. Most of the waters sampled, however, are enriched in Ca relative to evaporating sea water. The waters most enriched in Ca are BC-6, BC-8, CS-1, M-1 and M-3 located along the margins of the study area. Samples BC-9, BC-12, BC-13, and TB-1 from the central and north-central portions of the study area are slightly depleted in Ca (Fig. 15). The Ca/Cl ratio of the oil-field waters bears no relation to the formation under the Lansing-Kansas City Groups (Fig. 15) or the production zone within the Lansing-Kansas City Groups (Fig. 16).

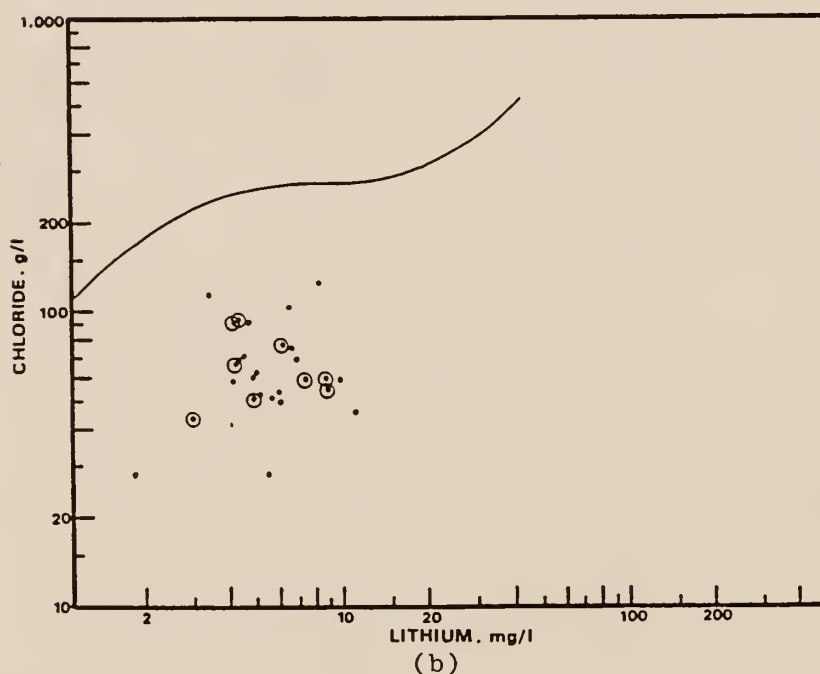
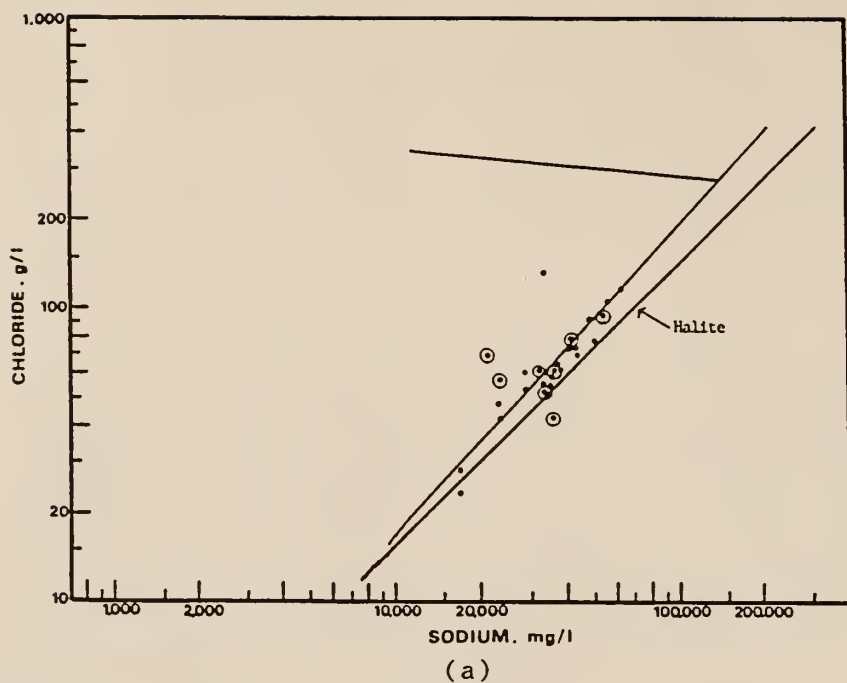
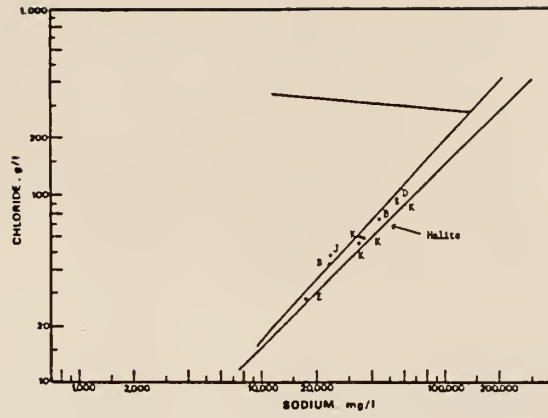
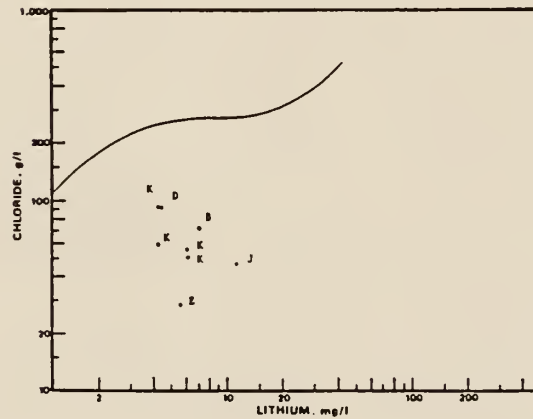


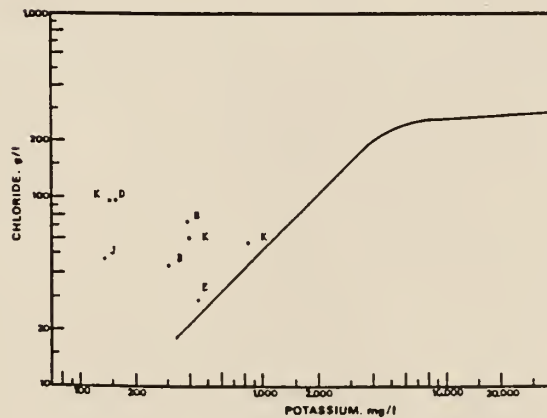
Figure 12. Comparison of concentrations in Lansing-Kansas City oil-field waters, western Kansas with evaporating sea water. Solid line represents sea water evaporation curve: a) Cl vs Na and b) Cl vs Li (samples marked by circles denote Lansing-Kansas City Groups underlain by Cambro-Ordovician strata, all others underlain by Pennsylvanian-Mississippian strata; modified from Collins, 1974).



(a)



(b)



(c)

Figure 13. Comparison of concentrations in Lansing-Kansas City oil-field waters, western Kansas, by production zone, with evaporating sea water. Solid line represents sea water evaporation curve: a) Cl vs Na, b) Cl vs Li, and c) Cl vs K (modified from Collins, 1974).

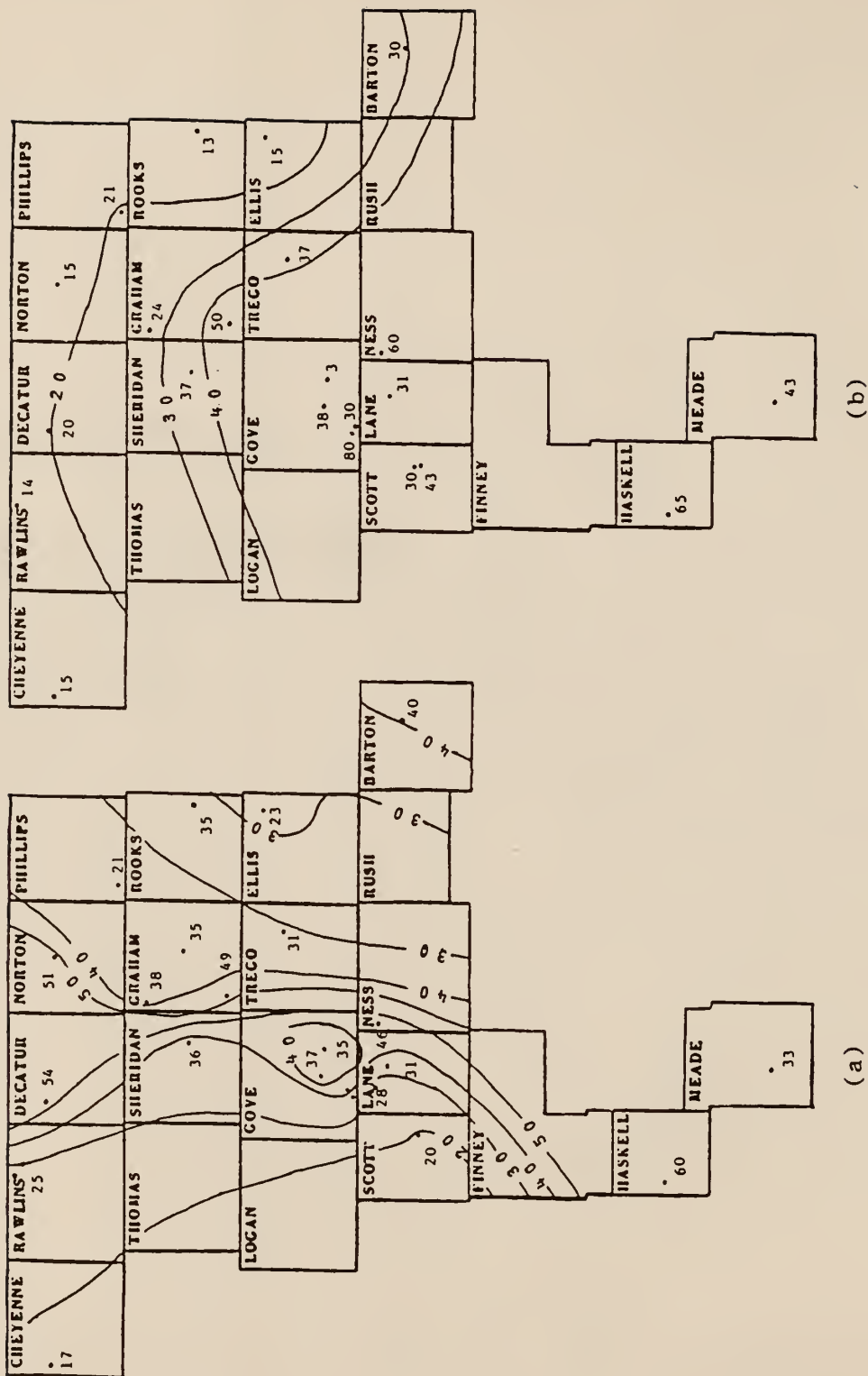
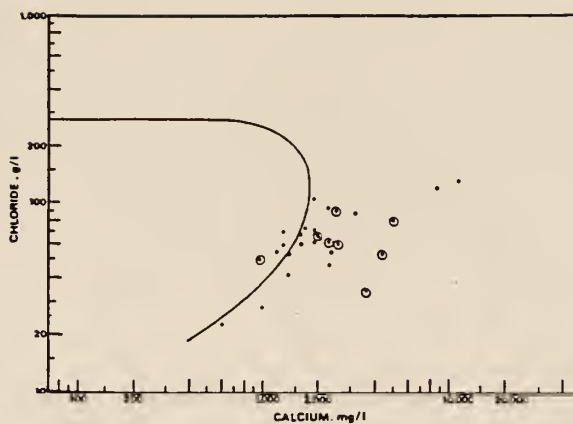
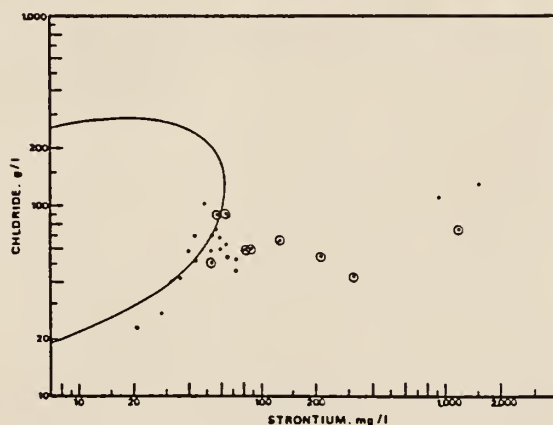


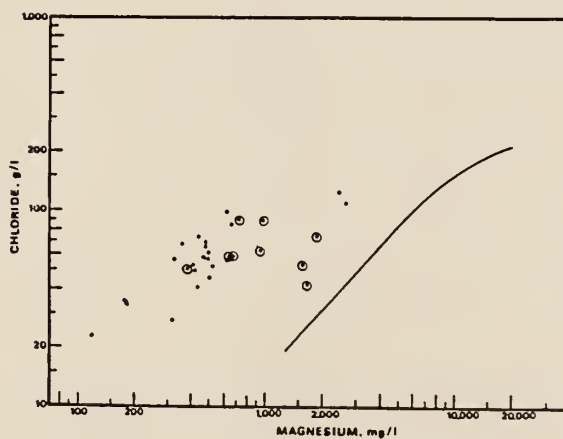
Figure 14. Spatial distribution of concentrations over the study area: a) Na X 1,000 and b) K X 10 (mg/l).



(a)

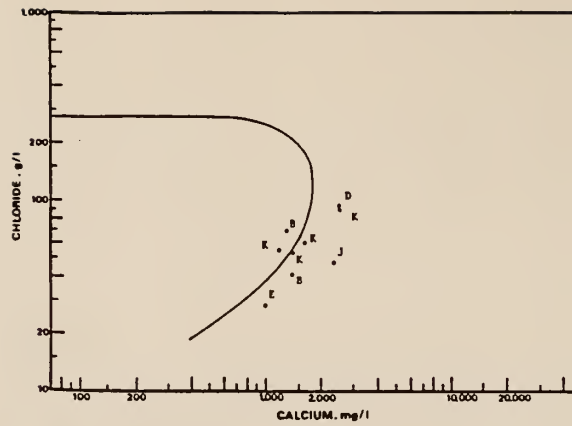


(b)

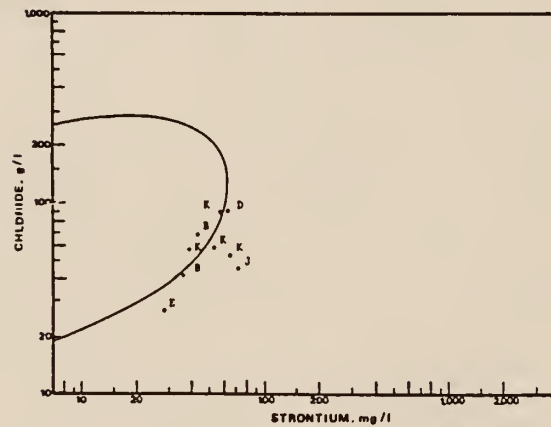


(c)

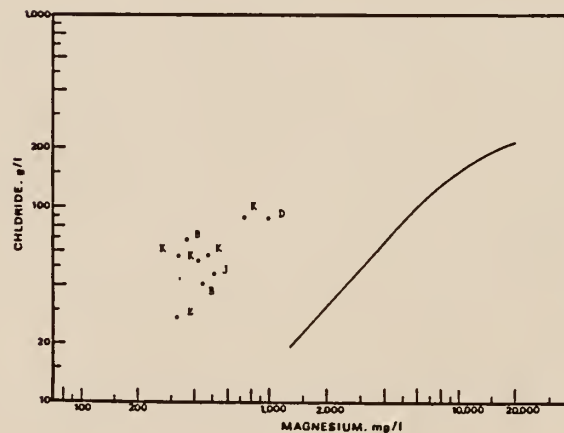
Figure 15. Comparison of concentrations in Lansing-Kansas City oil-field waters, western Kansas with evaporating sea water. Solid line represents sea water evaporation curve: a) Cl vs Ca, b) Cl vs Sr, and c) Cl vs Mg (for explanation of symbols, see Fig. 12; modified from Collins, 1974).



(a)



(b)



(c)

Figure 16. Comparison of concentrations in Lansing-Kansas City oil-field waters, western Kansas, by production zone, with evaporating sea water. Solid line represents sea water evaporation curve: a) Cl vs Ca, b) Cl vs Sr, and c) Cl vs Mg (modified from Collins, 1974).

Strontium enrichment relative to normal evaporating sea water is seen in many of the oil-field waters, though several samples plot close to the sea water evaporation line and a few are slightly depleted in Sr (Fig. 15). The samples most enriched in Sr (BC-6, BC-8, CS-1, M-1, and M-3) are also the samples least depleted in Mg and, with the exception of CS-1, the samples most enriched in Ca. Several samples plot very close to the sea water evaporation curve and BC-13, P-4, and VR-7 are depleted in Sr relative to evaporating sea water (Fig. 15). Once again, no trend can be seen between the Sr/Cl ratio and the formation below the Lansing-Kansas City Groups (Fig. 15) or the production zone (Fig. 16).

When compared to the Mg/Cl ratio of evaporating sea water, all of the oil-field waters are depleted in Mg (Fig. 15). The least depleted samples are BC-6, BC-8, CS-1, M-1, and M-3 from the eastern and southern regions of the study area. The chemistry is not significantly affected by the formation below the Lansing-Kansas City Groups (Fig. 15). The oil-field waters did not show any zonal preference to Mg depletion (Fig. 16).

The spatial distributions of Ca, Sr, and Mg concentrations over the study area exhibit similar trends (Fig. 17). The highest Ca, Sr, and Mg concentrations occur in the south and southeast portions of the study area, whereas the concentration of each of these decreases toward the northwest.

The oil-field waters are all enriched in Li relative to evaporating sea water, and plot in a fairly close cluster (Fig. 12). The least-enriched samples CS-1 and CS-4 from the northeast and

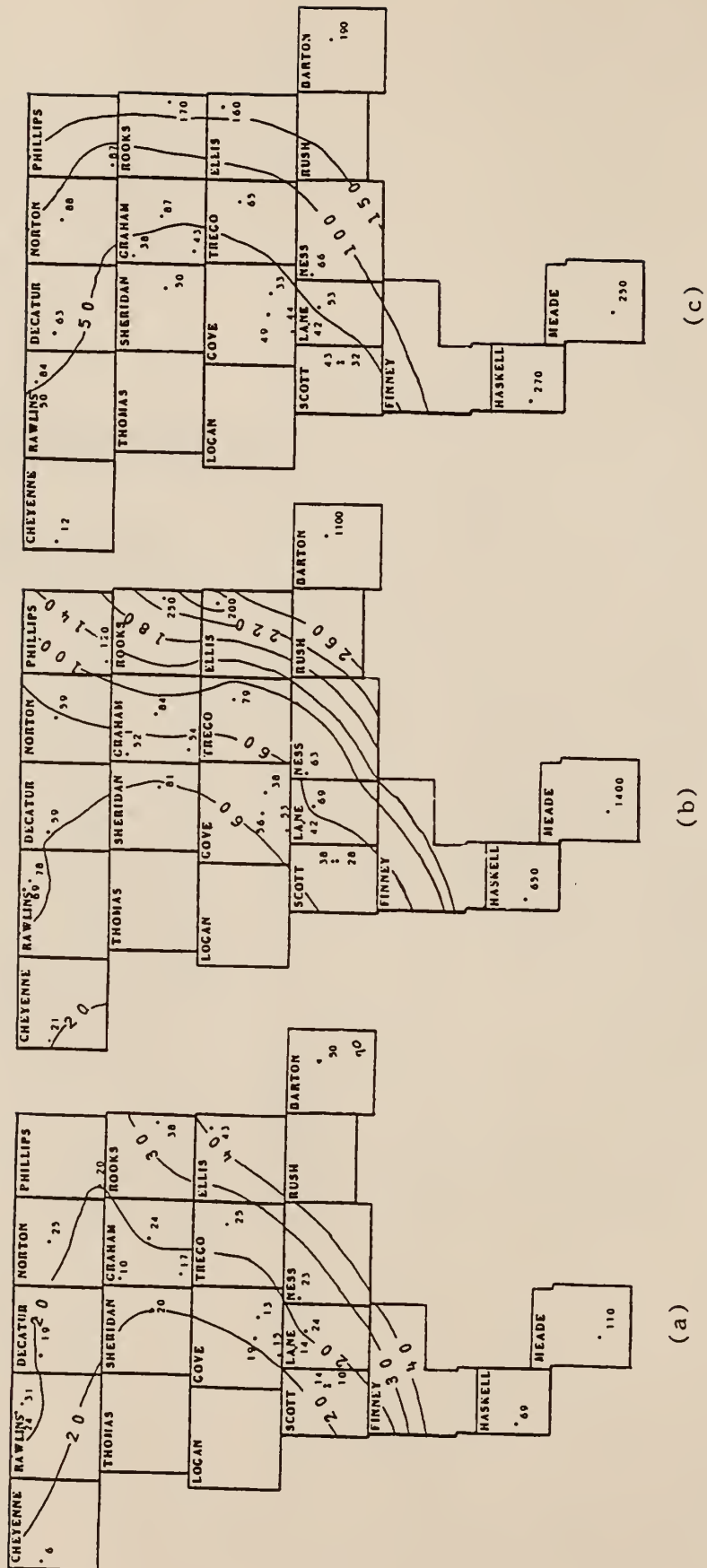


Figure 17. Spatial distribution of concentrations over the study area: a) Ca X 100, b) Sr, and c) X 10 (mg/l).

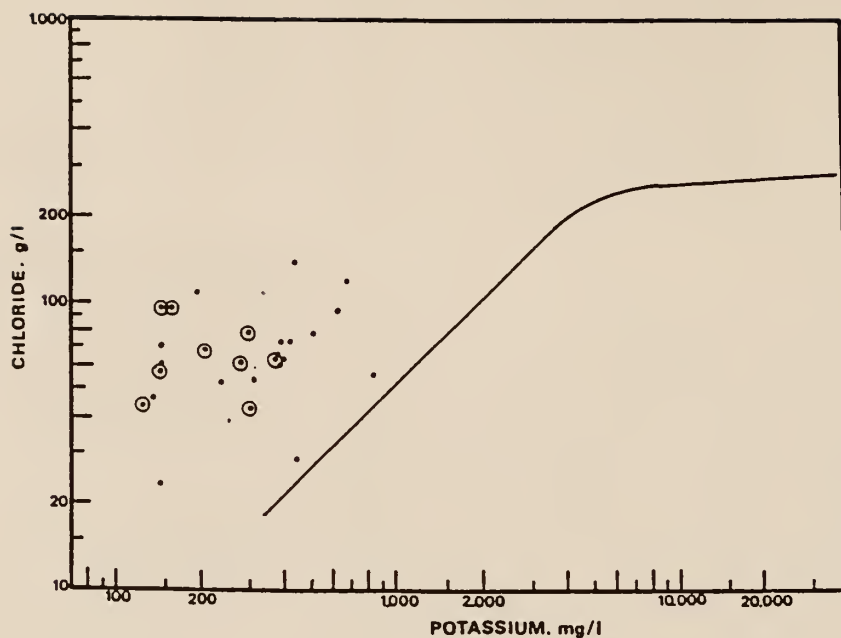
northwest portions of the study area respectively, plot somewhat apart from the rest of the samples. These same two are the only samples enriched in Na and both are among the most depleted in K. Neither the underlying formation nor the different producing zones within the Lansing-Kansas City Groups shows any correlation with the Li/Cl ratio (Fig. 12; Fig. 13).

All of the oil-field waters are depleted in K relative to evaporating sea water (Fig. 18). The K/Cl ratios of the waters are fairly widely distributed and are not controlled by the formation underlying the Lansing-Kansas City Groups (Fig. 18). Also, no zonal trend can be seen (Fig. 13).

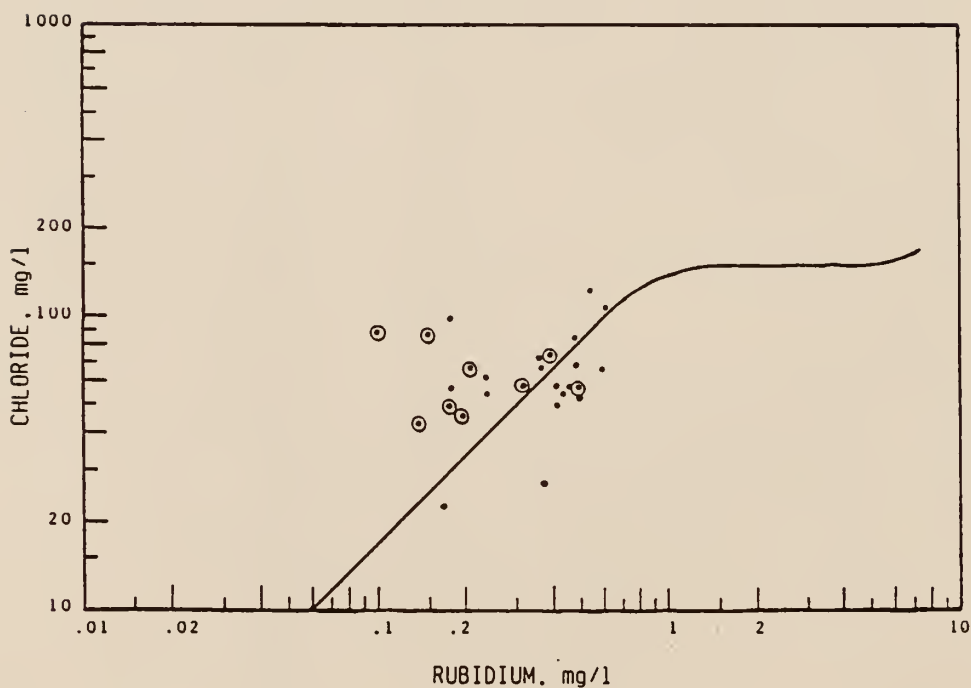
The K concentration varies greatly over the study area (Fig. 14). The lowest concentrations are present in the northeast and northwest portion of the study area. No general trend can be seen in the southern area.

Most of the water samples plot fairly close to the Rb/Cl line for evaporating sea water with approximately half of the samples slightly enriched and half slightly depleted in Rb (Fig. 18). In general, the samples located along the northern, eastern, and southern margins of the study area are depleted in Rb. No relation of Rb/Cl ratio to the underlying formation can be seen (Fig. 18).

When compared to evaporating sea water, the oil-field waters are all depleted in SO_4 except for BC-15 and CS-4 located in the central and northwest portions of the study area, respectively (Fig. 19). Samples BC-6, BC-8, CS-1, CS-2, M-1, and M-3, taken from the eastern and southern margins of the study area, are the most depleted in SO_4 .



(a)



(b)

Figure 18. Comparison of concentrations in Lansing-Kansas City oil-field waters, western Kansas with evaporating sea water. Solid line represents sea water evaporation curve: a) Cl vs K and b) Cl vs Rb (for explanation of symbols, see Fig. 12; modified from Collins, 1974).

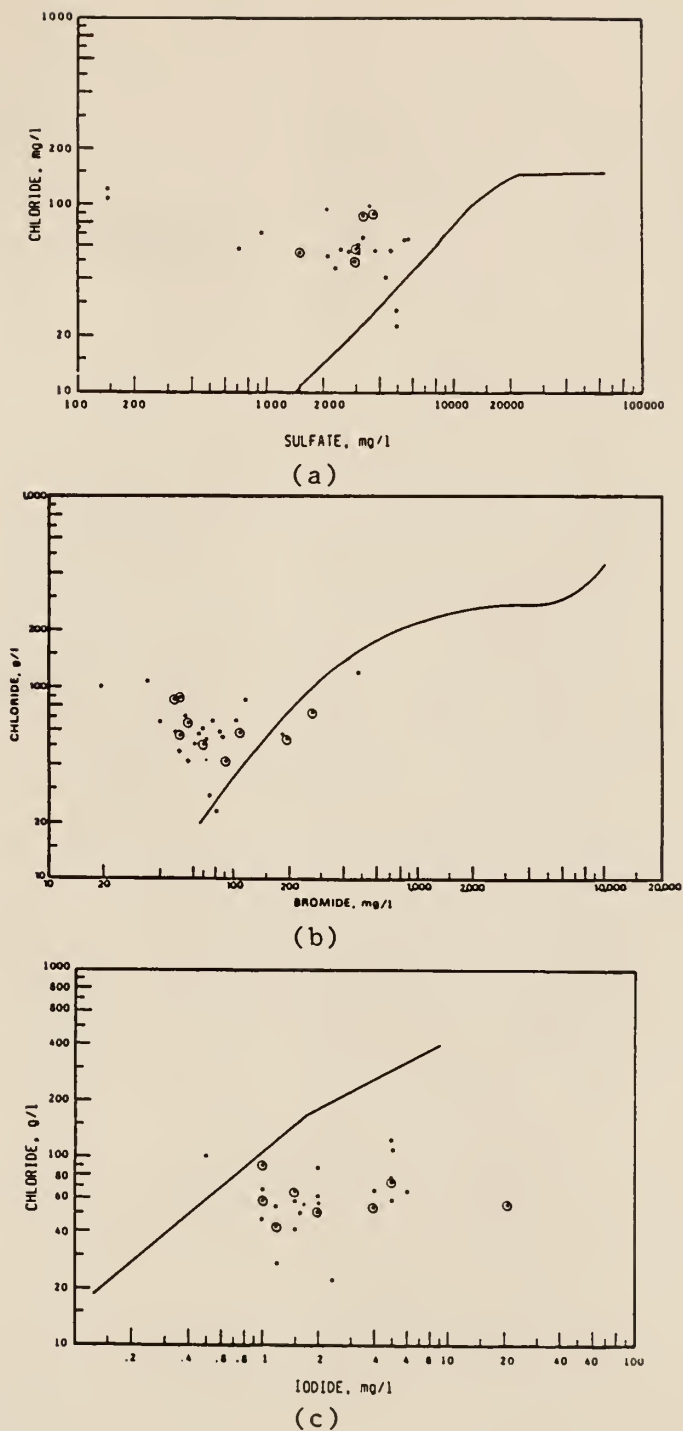


Figure 19. Comparison of concentrations in Lansing-Kansas City oil-field waters, western Kansas with evaporating sea water. Solid line represents sea water evaporation curve: a) Cl vs SO_4 , b) Cl vs Br, and c) Cl vs I (for explanation of symbols, see Fig. 12; modified from Collins, 1974).

The formation under the Lansing-Kansas City Groups is not significantly affecting the SO_4/Cl ratio (Fig. 19).

When compared to evaporating sea water, all of the oil-field waters are depleted in Br, except for BC-6, BC-8, CS-4, M-1, and P-4 which plot close to the evaporite curve but are slightly enriched in Br (Fig. 19). With the exception of P-4, these are the same waters found to be least depleted in Mg and most enriched in Ca and Sr. The Br/Cl ratio shows no preference to underlying formation (Fig. 19) or production zone (Fig. 20).

The oil-field water samples are all enriched in I relative to evaporating sea water except for VR-7 which is also the sample most depleted in Br (Fig. 19). Sample BC-1 is much more enriched in I than the remaining samples. The formation below the Lansing-Kansas City Groups does not seem to control the Br/Cl ratio (Fig. 19). There is no zonal trend to the I/CL ratio (Fig. 20).

ISOTOPIC DATA OF WATERS

Oxygen and Hydrogen Isotopic Data

A few water samples were selected for stable isotopic analyses of oxygen and hydrogen. The relative abundances of the different isotopes of each element were measured and compared to the corresponding value of standard mean ocean water (SMOW) by the equation:

$$\delta^{18}\text{O}_{\text{sample}} = \frac{(\text{}^{18}\text{O}/\text{}^{16}\text{O})_{\text{sample}} - (\text{}^{18}\text{O}/\text{}^{16}\text{O})_{\text{SMOW}}}{(\text{}^{18}\text{O}/\text{}^{16}\text{O})_{\text{SMOW}}} \times 1000.$$

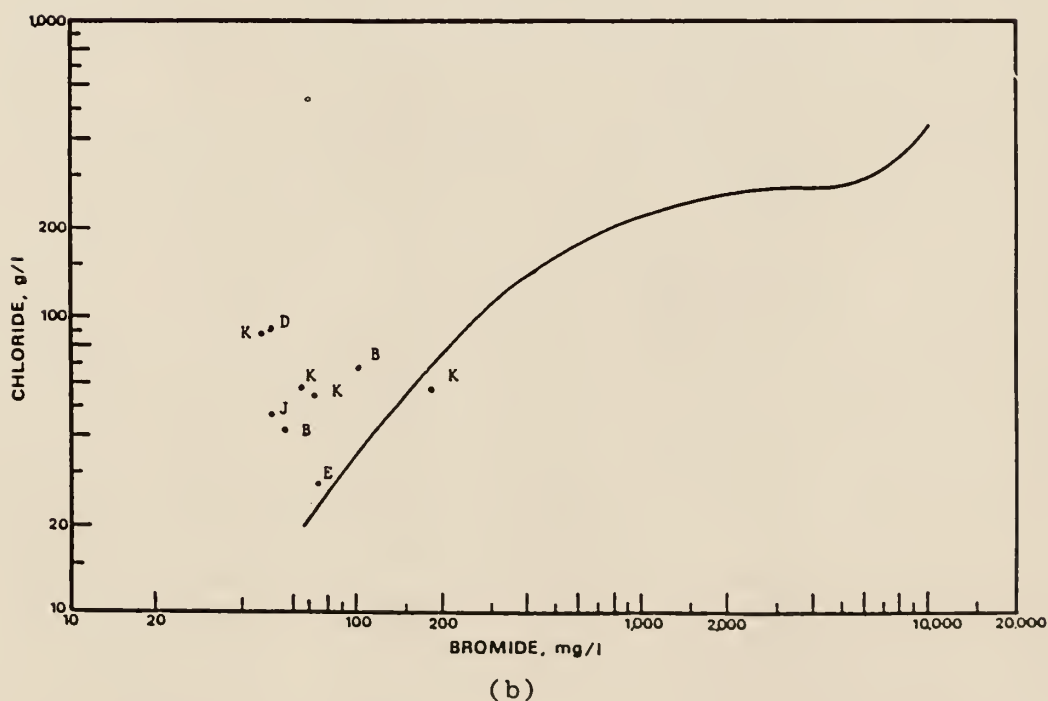
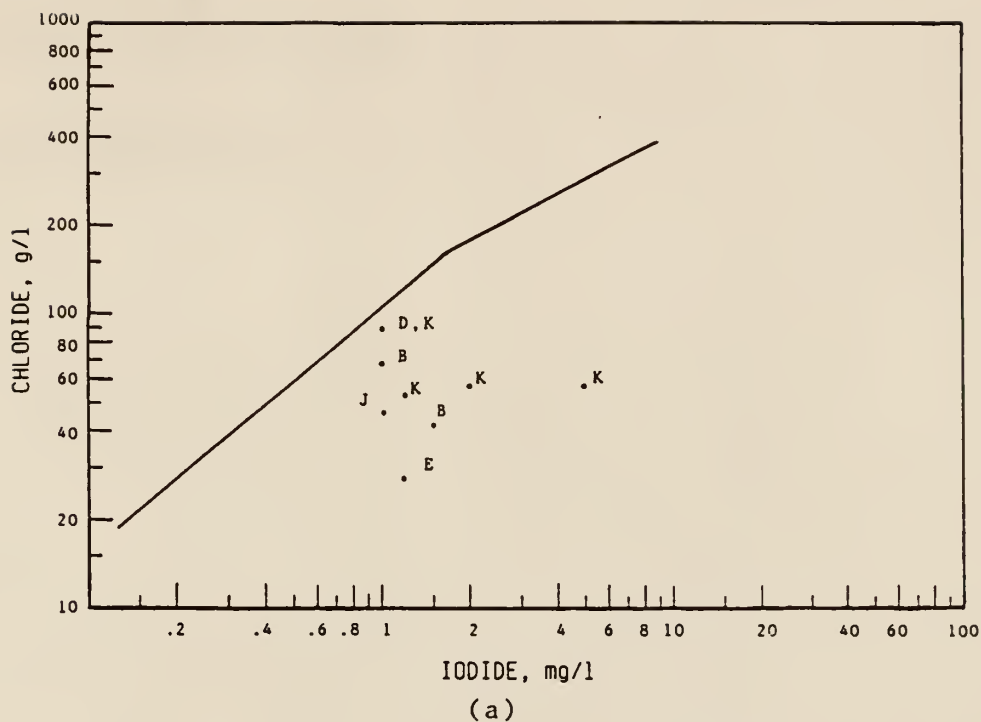


Figure 20. Comparison of concentrations in Lansing-Kansas City oil-field waters, western Kansas, by production zone, with evaporating sea water. Solid line represents sea water evaporation curve: a) Cl vs I and b) Cl vs Br (modified from Collins, 1974).

The value of δD_{sample} can be similarly expressed by substituting D/H, for the sample, in the above equation. The results, presented in Table 8., are expressed in per mil (‰).

The δD values of the oil-field waters were all negative between -64 per mil and -16 per mil, the most highly negative values being located in the northern and eastern portions of the study area (Fig. 21). The least negative value was in M-1 (-16 ‰) which is the southern-most sample. The D-isotopic composition of the waters does not appear related to the zone of production (Table 8).

There are both positive and negative deviations in the $\delta^{18}O$ values which are between -7.5 per mil and +10.3 per mil. The most positive values, in samples BC-15 (+10.3 ‰) and BC-8 (+8.4 ‰), are from the southcentral and southeastern portions of the study area, respectively. There are areas of lower $\delta^{18}O$ values in the eastern and northern portions of the study area (Fig. 21). The O-isotopic composition of the waters does not appear related to the zone of production (Table 8).

Strontium Isotopes

The Sr isotopic values are presented in Table 9. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the oil-field waters range mostly between 0.70882 and 0.71027, with the exception of three high values for samples BC-10 (0.71119), VR-5 (0.71135), and BC-1 (0.71506). The higher values occur in a northwest to southeast trending path through the study area. The lowest values are located in the southern portion of the study area (Fig. 22). There appears to be no correlation between

Table 8. Stable isotopic analyses of Lansing-Kansas City oil-field waters, western Kansas.
(concentrations expressed in per mil SMOW)

<u>Sample</u>	<u>δD</u>	<u>$\delta^{18}O$</u>	<u>Production Zone</u>
BC-1	-62.0	-6.2	A,F
BC-6	-57.0	-6.2	A,C
BC-8	-22.0	+8.4	---
BC-10	-38.0	+2.4	B,C,H,J
BC-15	-26.0	+10.3	E
M-1	-16.0	+3.3	---
M-3	-30.0	+0.1	---
P-4	-45.0	-1.1	K
VR-5	-64.0	-5.1	---
VR-13	-58.0	-2.2	D
CS-1*	-63.0	-7.5	A,B,D
CS-4*	-46.0	+1.6	A,J

* - These waters are Cl-Mg Type, the remainder are Cl-Ca Type.

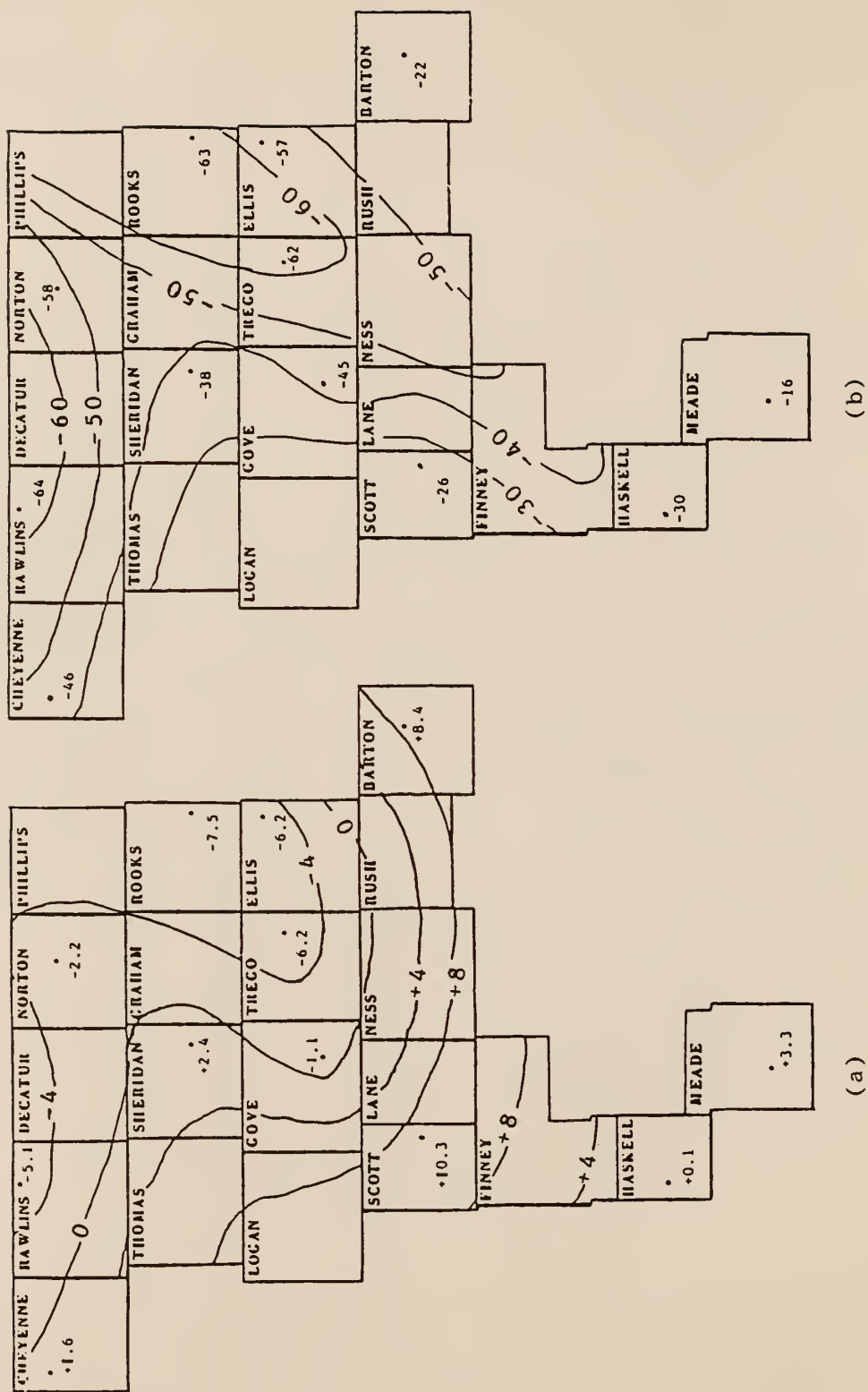


Figure 21. Spatial distribution of values over the study area: a) $\delta^{18}\text{O}$ and b) δD .

Table 9. Strontium isotopic composition of Lansing-Kansas City oil-field waters, western Kansas.

<u>Sample</u>	<u>Sr</u>	<u>$^{87}\text{Sr}/^{86}\text{Sr}$</u>
BC-1	79	0.71506
BC-3	56	0.70936
BC-4	52	0.70884
BC-6	200	0.71001
BC-10	61	0.71119
BC-13	44	0.70884
BC-14	58	0.70918
BC-15	28	0.70905
CS-2	120	0.70930
M-1	1400	0.70880
M-3	850	0.70889
P-4	38	0.70933
TB-5	63	0.70885
VR-5	69	0.71135
VR-7	47	0.71027
VR-13	62	0.70998
BC-2*	54	0.70994
BC-9*	1100	0.70994
CS-1*	250	0.70882
CS-4*	21	0.70994

* - These waters are Cl-Mg Type,
the remainder are Cl-Ca Type.

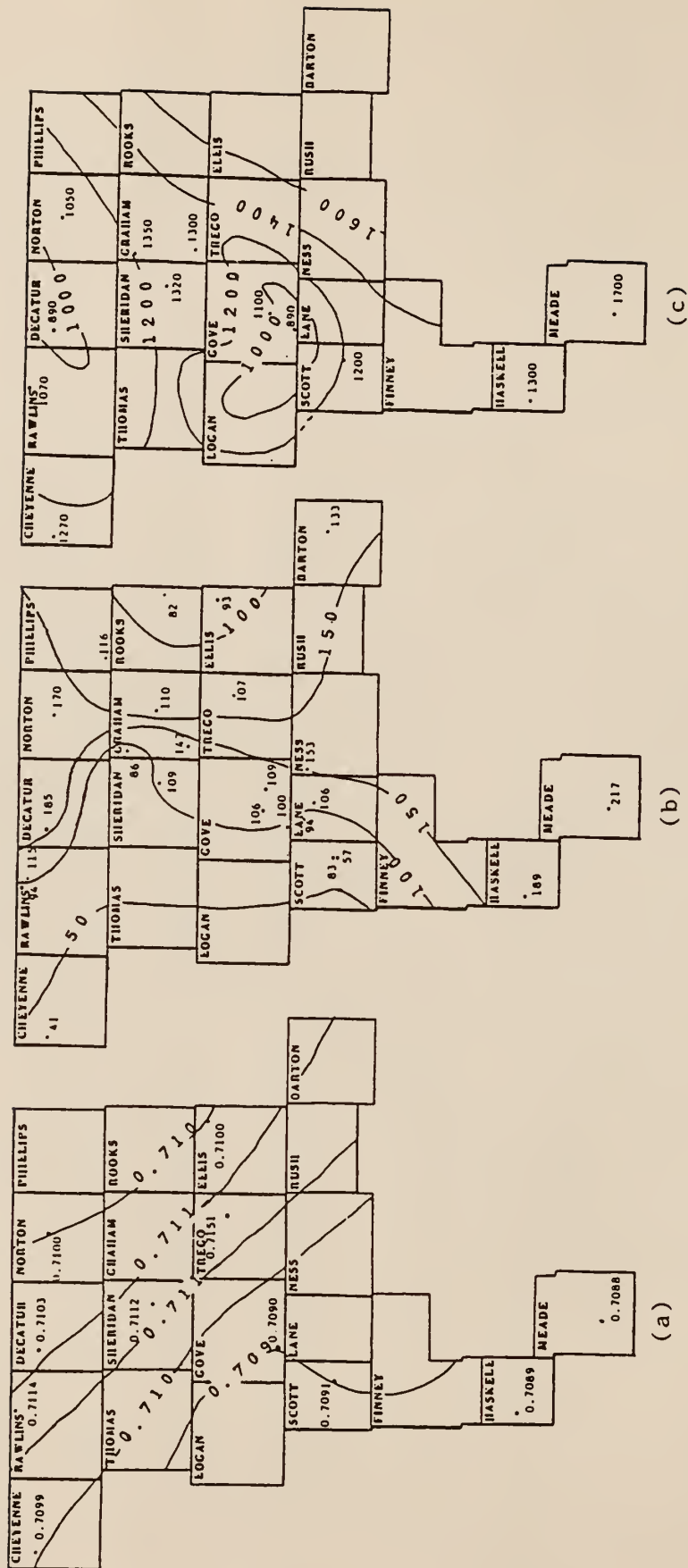


Figure 22. Spatial distribution of values over the study area: a) $^{87}\text{Sr}/^{86}\text{Sr}$, b) TDS X 1,000, and c) Bottom hole pressure.

$^{87}\text{Sr}/^{86}\text{Sr}$ ratio and either Rb, Sr, or Li content of the oil-field waters or the production zone (Table 9).

PETROGRAPHY

Carbonates

Sample 3, taken from the Lansing-Kansas City J-zone, is a very fossiliferous biosparite with recrystallized non-ferroan calcite forming the ground mass. Solution cavities with irregular boundaries are present within the non-ferroan calcite that have been filled with ferroan calcite. A small amount of dolomite is present, but only within the non-ferroan ground mass.

The bioclastic limestone of core 4 contains crinoids, forams, and brachiopods in a recrystallized non-ferroan ground mass. This biosparite, taken from the D-zone, contains numerous microstylolites. These are easily seen due to the pressure solution removing the carbonate while the clays remain forming dark bands. The microstylolites seem to have acted as planes of weakness along which solutions have passed, producing dolomitization. In places the original rock fabric has been isolated by extensive dolomitization. This limestone shows no evidence of solution. Within the cavity of a brachiopod, two stages of cement can be seen. The first stage consists of blades of non-ferroan calcite growing toward the center of the cavity. The second stage fills the remainder of the cavity with ferroan calcite. This is the only ferroan calcite present in this sample.

Core sample 5, taken from the H-zone, is a biosparite and is virtually made up of non-ferroan calcite with significant amounts of discrete dolomite occurring throughout the ground mass. Fossil cavities are also filled with non-ferroan calcite and no solution cavities are present. However, a small amount of pyrite is present in the core sample.

Sample 6 is a massive recrystallized sparite with a few fossils present as shell debris. The ground mass is composed of non-ferroan calcite. Irregularly shaped cavities are present indicating solution activity. These cavities are filled with material that exhibits some zonation. Most of the volume of each cavity is filled with ferroan calcite, within which there is also some non-ferroan calcite.

Core sample 7, a biosparite taken from the J-zone, is composed of a recrystallized non-ferroan calcite ground mass. Dolomite is very abundant in this material but none is present within the solution-cavity fills that are composed of ferroan calcite.

Sample 8, A-zone material, has a ground mass similar to that of the other core samples but contains almost no fossils. Irregularly shaped solution cavities contain two generations of cement. Ferroan calcite is present around the edges of the cavities with non-ferroan calcite in the central portions.

Shales

Difficulties arise when determining the relative amounts of minerals from x-ray diagrams. These are due to differences in mass absorption coefficients of the minerals, variations in chemical and

structural composition, orientation, sample preparation, and the quantification method used (Lee, 1972). The relative abundances of the minerals present in each shale sample were determined following the method outlined by Maikem and Campbell (1965).

The mineralogic composition of the shales are predominantly illite (Table 10). Illite ranged from 63 percent in sample 11 to 91 percent in sample 12. A small amount of mixed-layer clay is present (2-7%) in all of the samples. This mixed layer clay is composed of illite-chlorite or illite-smectite. Kaolinite and chlorite contents varied in the shales and often only one of these was present in a particular sample. The relative abundances of kaolinite and chlorite were as much as 7 percent, except for sample 11 which contained 24 percent chlorite. Sample 11 also had an unusually high amount (approximately 33 percent) of smectite.

DISCUSSION

POTENTIOMETRIC CONFIGURATION

The U.S. Geological Survey is currently conducting a study of the regional hydrochemistry of aquifer systems underlying the Mid-continent region including Kansas. Baker and Leonard (in press) have estimated the apparent direction of lateral flow near the centerline of a geohydrologic unit, consisting of rocks belonging to the Pennsylvanian System, based on pressure and density data. The flow direction in this unit is generally west to east across Kansas. The

Table 10. Mineralogy of shale samples collected from Lansing-Kansas City cores.
(values in percent)

<u>Sample</u>	<u>Size(microns)</u>	<u>Illite</u>	<u>Mixed Layer</u>	<u>Kaolinite</u>	<u>Chlorite</u>	<u>Smectite</u>
10	2.0 - 0.2	89	3	0	8	0
	<0.2	92	3	2	3	0
11	2.0 - 0.2	67	4	5	24	0
	<0.2	59	2	3	3	33
12	2.0 - 0.2	89	2	9	0	0
	<0.2	93	2	5	0	0
13	2.0 - 0.2	76	7	0	17	0
	<0.2	84	2	7	7	0
14	2.0 - 0.2	89	3	0	8	0
	<0.2	90	3	4	3	0

Lansing-Kansas City Groups which occur near the center of the Pennsylvanian strata should exhibit this general flow pattern.

Pressure on fluid within the subsurface is measured when drilling an oil well and recorded on scout cards as bottom hole pressure. A contour of bottom-hole pressure was constructed for the Lansing-Kansas City Groups. Using the small number of control points available, a region of lower pressure appears to be present within the study area (Fig. 22). The lower pressure in this area may allow cross-formational flow from adjacent units. In this location, waters from adjacent strata mixing with Lansing-Kansas City water could be affecting the chemistry of the oil-field waters.

MAJOR CHEMISTRY

Most of the oil-field waters contain an excess amount of Cl with respect to Na and Mg. Waters having these characteristics are classified as Cl-Ca Type, and they are thought to occur in deeper zones of basins that are isolated from the influence of infiltration by meteoric waters. These areas are thought to be nearly hydrostatic.

A few of the waters (BC-2, BC-9, CS-1, and CS-4) from the northeastern and northwestern portion of the study area are Cl-Mg Type. Waters of this type are thought to be representative of the transition zone between the deeper, hydrostatic portions of the basin and the shallower, hydrodynamic portion (Collins, 1975). These water samples may represent areas affected by meteoric water mixing with water already present within the reservoir rocks. The O- and D-isotopic data, discussed below, indicate that a meteoric water

component is present in the waters. Also, secondary porosity in the Lansing-Kansas City strata, in northern Kansas, has been attributed to meteoric water influx (Heckel, 1977, 1984, 1985, and 1986; Watney, 1980 and 1985).

The chemical content of oil-field water can potentially be modified within the subsurface by processes including: evaporation, mixing with other waters, ion exchange with minerals, mineral dissolution and precipitation, biologic activities, and ultrafiltration through shale membranes. Ultrafiltration through shale membranes, could partially control ion concentrations in the Lansing-Kansas City oil-field waters. The study area is located within the Hugoton Embayment, which is a shelf-like extension of the deeper Anadarko Basin to the south. The pressures in the study area may be insufficient to produce local ultrafiltration through shale membranes. Though shale membrane filtration may have occurred, this process will not be considered here.

In the discussion to follow, all of the ion concentrations have been compared to those of evaporating sea water at the same Cl level. Based on this comparison, the waters are referred to as being enriched or depleted in a specific ion.

Sodium

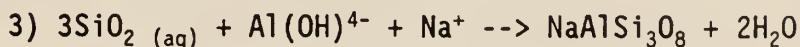
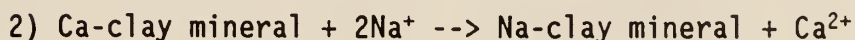
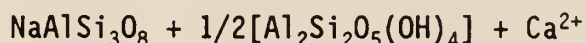
Most of the oil-field waters' Na/Cl ratios are close to the Na/Cl equivalent ratio of halite or that of sea water in its early stage of evaporation (Fig. 12). One possible mechanism to produce this distribution along the trend of the halite line is the dissolution of

varied amounts of halite, possibly from overlying Permian salt beds. The stable isotopic data, which is discussed below, indicates that this water is composed of a mixture of meteoric water, gypsum hydration water, and sea water or evaporated sea water. The dissolution of halite by this water would add Cl, thus causing all ions except for Na to appear depleted or less enriched.

A few samples from the eastern and southern portions of the study area (BC-6, CS-2, M-1, and M-3) appear depleted in Na, so a process resulting in relative Na depletion may have occurred. Sodium loss has been commonly attributed to: 1) conversion of anorthite to albite plus kaolinite, 2) ion exchange by clay minerals, 3) formation of albite, and 4) conversion of K-feldspar to Na-feldspar (Carpenter, 1978). The above reactions may be described as follows:



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However, none of the above mechanisms appears to be satisfactory in

explaining the Na depletion found in some of the water samples from the Lansing-Kansas City Groups for the following reasons.

Anorthite is yet to be found in sedimentary sequences in this region although Precambrian basement rocks in the area include some mafic crystalline rocks. To produce the amount of Na reduction necessary, reaction 1 (above) would require a large source of SiO_2 . Therefore, this reaction may not significantly contribute to Na depletion in these waters. Moreover, reaction with Precambrian crystalline rocks would most likely cause the waters to be enriched in ^{87}Sr . But, the Na-depleted waters are not any more enriched in ^{87}Sr than the remaining waters.

Ion exchange by clay minerals, represented by equation 2, would also tend to increase the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the waters. If the Na depletion observed in the four water samples mentioned were due to ion exchange with clay minerals, these waters should possess high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. As the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of samples M-1 and M-3 are lower than those of most of the waters analyzed, this process of clay ion exchange does not appear to be a major factor in the Na depletion.

Alkali feldspars have been found in Pennsylvanian shales within the study area (Chaudhuri, personal communication, 1987) but neither the amount nor the origin of these feldspars has been investigated. Even considering that some of these feldspars having Na in their compositions were diagenetic in origin, the Si removal from the solution would be much higher than the Na removal. Consequently, one may expect to find the Si depletion corresponding in some extent to the Na depletion. But, this was not the case with the Na depleted

waters in the Lansing-Kansas City Groups. Also, feldspars tend to incorporate some amount of Li into their structures. The Na depleted waters were not among those least enriched in Li. Thus, it appears this process of diagenetic formation of alkali feldspars did not produce the observed Na depletion.

The removal of Na by albitization of K-feldspar would cause enrichment of K in the waters. As all of the water samples were depleted in K and the Na depleted waters were no less depleted in K than the others, the albitization process does not appear to be an important factor for the Na depletion of the waters.

Sodium depletion can be explained by the mixing of highly evaporated sea water with much less-evaporated sea water or with meteoric water. Evaporation of sea water increases the Na and Cl concentrations at a constant ratio until precipitation of halite begins, at which time, the Na/Cl ratio begins to decrease. This Na-Cl evaporation curve is shown in Figure 12. Evaporated sea water that has been concentrated to the point of halite precipitation could mix with less concentrated sea water or meteoric water to produce a water whose Na/Cl ratio would fall below, and to the left of, the sea water evaporation line. By this process, apparent Na depletion can be achieved in the anomolous samples. Thus, mixing of waters having different origins argues to be the best explanation for Na depletion.

The mixing processes proposed above will not explain the slightly enriched Na concentration of sample CS-1 and possibly sample CS-4 from the northeast and northwest portions of the study area, respectively. Recall that the dissolution of halite from evaporite deposits in the

overlying Permian formations probably produced the constant Na/Cl ratios and some other chemical characteristics of the oil-field waters. These evaporites could also locally contain non-Cl, Na-rich salts such as glauberite ($\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$) and blodite ($\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$). These salts could dissolve along with NaCl locally from the overlying evaporite deposits causing the waters to become enriched in Na and SO_4 . Sample CS-1 is among the least depleted in Mg which may be due, at least in part, to the dissolution of Na-Mg- SO_4 salts. Sample CS-4 is enriched in SO_4 which may be evidence for the proposed reaction. Sample CS-1 is very depleted in SO_4 but this could have been due to subsequent SO_4 removal by precipitation or organic reduction. Late-stage salts such as glauberite and blodite contain larger amounts of Br than earlier precipitated salts. Thus, dissolution of these salts could explain the large Br concentrations of these two waters.

Bromide

Most of the oil-field waters are depleted in Br (Fig. 19). Dissolution of Br-depleted recrystallized halite, by one of the water components in the mixing model, could explain the low Br values present in the majority of the water samples. Bromide is essentially free from precipitation reactions and hence removal of Br from the waters by such a process seems unlikely.

Five oil-field water samples (BC-6, BC-8, CS-4, P-4 and M-1) appear slightly enriched in Br. Highly evaporated sea water mixing with less evaporated sea water or meteoric water could produce the Br

characteristics of these waters. The mixed water origin for the oil-field waters appears tenable from the stable isotopic data, and the same mixing process can reasonably explain the Na data of the waters.

Magnesium, Calcium, and Strontium

The oil-field waters are all depleted in Mg and most are enriched in Ca and Sr (Fig 15). A few waters are also depleted in Sr and Ca. Dissolution of halite in a model of mixed water has been suggested as an explanation for the Na characteristics of most of the waters. The Cl increase is likely to make elements other than Na appear depleted. The dissolution process can provide an explanation for the Mg-Ca-Sr relationships of only a few of the oil-field water samples. This does not explain why most of the waters are enriched in Ca and Sr while being depleted in Mg. The antipathy between Mg and Ca or Sr in waters is commonly attributed to either chloritization or dolomitization during water-rock interactions. The reactions are described as:



Both processes are plausible for the Mg-Ca-Sr characteristics of the Lansing-Kansas City oil-field waters.

Chlorite has been found to be as much as 24 percent of the clay minerals in shales from the Lansing-Kansas City Groups. Due to radiogenic ^{87}Sr in clay minerals, this reaction could cause the

$^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the waters to be increased. In view of the generally non-radiogenic Sr isotopic characteristics of the oil-field waters which are discussed below, the formation of chlorite may not be an important controlling factor for the Mg-Ca-Sr relationships of the waters.

Dolomite was found in all of the Lansing-Kansas City core samples examined. The distribution of dolomite varied from widely scattered grains to concentrated zones along microstylolites. Investigation of Lansing-Kansas City strata and its cement stratigraphy in northern Kansas indicates that dolomite averages approximately 10 percent in the rocks of the Lansing-Kansas City Groups (James Anderson, personal communication, 1987). The amounts of dolomite present in Lansing-Kansas City rocks in the subsurface in the central and southern parts of the study area are not known. However, considerable amounts dolomitic rocks have been reported for Paleozoic sequences in Kansas (Merriam, 1963). Based on this evidence, dolomitization appears to be a dominant factor for the Mg-Ca-Sr relationship of the waters.

Most of the water samples have Sr/Ca molar ratios between 1.0×10^{-2} and 3.0×10^{-2} and a few with values between 4.4×10^{-2} and 10.1×10^{-2} (from the southern and eastern portion of the study area). Should dolomitization become an important process for Mg depletion and Ca and Sr enrichments in these waters, their Sr/Ca molar ratios should be between 0.38×10^{-3} - 1.56×10^{-3} , from dolomitization of calcitic limestone and between 1.52×10^{-2} - 2.2×10^{-2} , from dolomitization of aragonitic limestone (Sass and Starinsky, 1979). However, the majority of the Sr/Ca molar ratios of the oil-field waters are between

these two sets of values for waters dolomitizing calcitic and aragonitic limestones. Three mechanisms may explain why the Sr/Ca molar ratios of the waters lie between these values: 1) water that has dolomitized calcitic limestone experiencing Sr addition by some process, 2) water that has dolomitized aragonitic limestone experiencing Sr depletion by some process, or 3) water dolomitizing calcitic and aragonitic limestone in varied amounts. Any of these mechanisms can explain the Sr/Ca molar ratios of the vast majority of the samples, but not all of them can explain the high Sr/Ca molar ratios above 2.2×10^{-2} found in some of the Lansing-Kansas City waters. These high ratios would require the addition of Sr to the waters. Thus, the most general process that will explain the Mg-Ca-Sr relationships of all the water samples would be dolomitization of calcitic limestone followed by addition of varied amounts of Sr to the waters.

A possible mechanism for Sr addition is the conversion of anhydrite to gypsum. The distribution coefficient of Sr in gypsum is less than that of anhydrite. Thus, conversion of anhydrite to gypsum, increasing the Sr content of the waters, may explain the high Sr/Ca molar ratios found in several of the waters. Vug-filling celestite deposits have been noticed in carbonate rocks from the southern part of the study area. This may indicate that subsequent Sr loss has occurred in some of the waters.

Lithium

The Lansing-Kansas City oil-field waters, like many other oil-field waters, were found to be enriched in Li (Fig. 12). Some of the major chemical attributes have been explained by mixing of highly evaporated sea water with less concentrated sea water or meteoric water. While mixing may contribute to the Li enrichment, the mixing process alone may not account for the total enrichment of Li in many of the water samples. Therefore, an additional process of Li enrichment is required. Some possible processes could be: 1) ion exchange with clay minerals, 2) conversion of smectite to illite or chlorite, and 3) reaction with carbonate reservoir rocks.

Lithium enrichment of oil-field waters has been frequently attributed to ion exchange with clay minerals (Collins, 1978). Lithium ions, because of their small size and thus large hydrated radii, are easily replaced in clay minerals by other alkali or alkaline earth ions. This can release Li to the waters.

Conversion of smectite to illite is another process which could account for the Li enrichment. Lithium is known to occupy the octahedral sites in smectite minerals and can be partially responsible for the location of charge deficiency in these sheets. During the conversion of smectite to illite, the primary seat of charge deficiency shifts from the octahedral to the tetrahedral sheet. The associated fluids may increase in Li during this conversion process. Similarly, due to chloritization of smectite, only Li in the interlayer site is likely to be replaced during the formation of the positively charged brucite sheet.

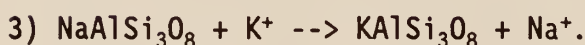
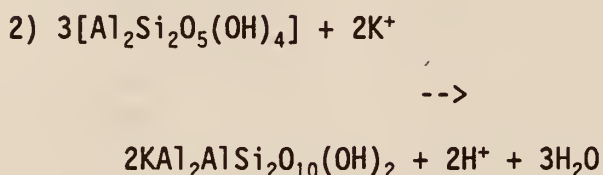
A third process that may produce Li enrichment is the reaction of the water with carbonate reservoir rocks. Billings and Ragland (1968) reported Li contents of approximately 3.9 ppm in reef carbonate sediments that contain no quartz or clay minerals. Considering that the distribution coefficient of Li in carbonate minerals is much less than 1×10^{-3} , (Chaudhuri, personal communication, 1987), extensive and repeated recrystallization of carbonate minerals by the waters could release considerable amounts of Li to the waters. Many of the Lansing-Kansas City oil-field waters have Sr isotopic compositions similar to that of marine Sr, and thus carbonate mineral recrystallization or dolomitization might have contributed to the Li enrichment of the waters.

The Li content of the Lansing-Kansas City waters can best be explained by mixing of waters accompanied by the recrystallization of carbonate minerals, since many of the waters have Sr isotopic compositions near the value of sea water. As many of the water samples have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios higher than sea water values, reactions with clay minerals may not be totally discounted to explain at least part of the Li enrichment.

Potassium

All of the waters are depleted in K (Fig. 18). Potassium depletion is common in oil-field waters. The addition of Cl by salt dissolution would cause the waters to appear depleted in K, though additional processes may also contribute to the depletion. A variety of processes have been proposed to explain K depletion which include:

1) conversion of kaolinite to K-feldspar, 2) conversion of kaolinite to illite, and 3) conversion of Na-rich feldspar to K-rich feldspar. These processes can be represented by:



The conversion of kaolinite to alkali-feldspar and illite in reactions 1 and 2, respectively, may also account for the K depletion of the waters. The H^+ produced by these reactions could be consumed by reactions with other minerals, particularly carbonate minerals. As mentioned previously, kaolinite is a very common clay mineral in the upper Paleozoic shales and sandstones of western Kansas. Mineral equilibria calculations based on a modified Dubey-Huckel equation were obtained from the U.S. Geological Survey at Rolla, Missouri for a few water samples (BC-6, BC-8, CS-1, CS-4, M-1, and M-3). This showed that the waters are in near saturation with respect to kaolinite, indicating that reactions with kaolinite to produce either feldspar or mica-like minerals is possible. Chaudhuri (personal communication, 1987) noted alkali-feldspar minerals in some of the Middle Pennsylvanian shales and also identified, from scanning electron

micrographs, growth of illite from kaolinite in Pennsylvanian Cherokee sandstones in western Kansas.

The conversion of Na-feldspar to K-feldspar may be accompanied by the release of radiogenic Sr to the waters. If this process caused the K depletion of the oil-field waters, the most K depleted waters should also have the most radiogenic Sr. This relationship is not observed. Therefore, reaction 3 was apparently not an important factor in the K depletion of the waters.

Rubidium

Approximately half of the samples are slightly enriched in Rb while the remainder are either slightly depleted in Rb or without any anomaly with respect to Rb concentrations (Fig. 18). The reactions proposed previously to explain K depletion could also account for the Rb depletion of the oil-field waters, although the conversion of kaolinite to albite would probably not deplete as much Rb as K.

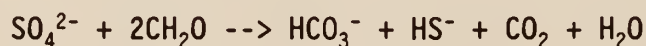
Rubidium enrichment has been found in other oil-field water studies (Broedel, 1983; Nicastro, 1983). Mixing of highly evaporated sea water with less concentrated sea water or meteoric water could be one explanation for the apparent enrichment. An additional process of Rb enrichment could be the conversion of carnallite to sylvite, which is expressed as:



The distribution coefficient of Rb in carnallite is greater than 1, whereas that in sylvite is much less than 1 (Kuhn, 1972). Primary carnallite may contain as much as 250 ppm Rb, whereas primary sylvite may contain as much as 50 ppm Rb. Thus, the conversion of carnallite to sylvite may release Rb causing Rb enrichment.

Sulfate

Two samples (CS-4 and BC-15) from the northern and central portions of the study area, respectively, are enriched in SO_4 relative to sea water (Fig. 19). This could have been accomplished by mixing of waters with different SO_4 contents, a process which has been proposed to explain various ion concentrations discussed previously. However, the SO_4 depletion shown by most samples could not have been achieved by mixing of different waters. As mentioned previously, the added Cl from halite dissolution would cause the SO_4 and other ions to appear depleted. But this Cl addition will not satisfactorily explain why SO_4 and Ca or Sr show a somewhat antipathetic relationship. In the southern and eastern portions of the study area some of the waters most depleted in SO_4 area also most enriched in Ca and Sr (Fig. 23). Additional SO_4 depletion could be due to sulfate reduction by bacteria. The reactions corresponding to this process are:



or



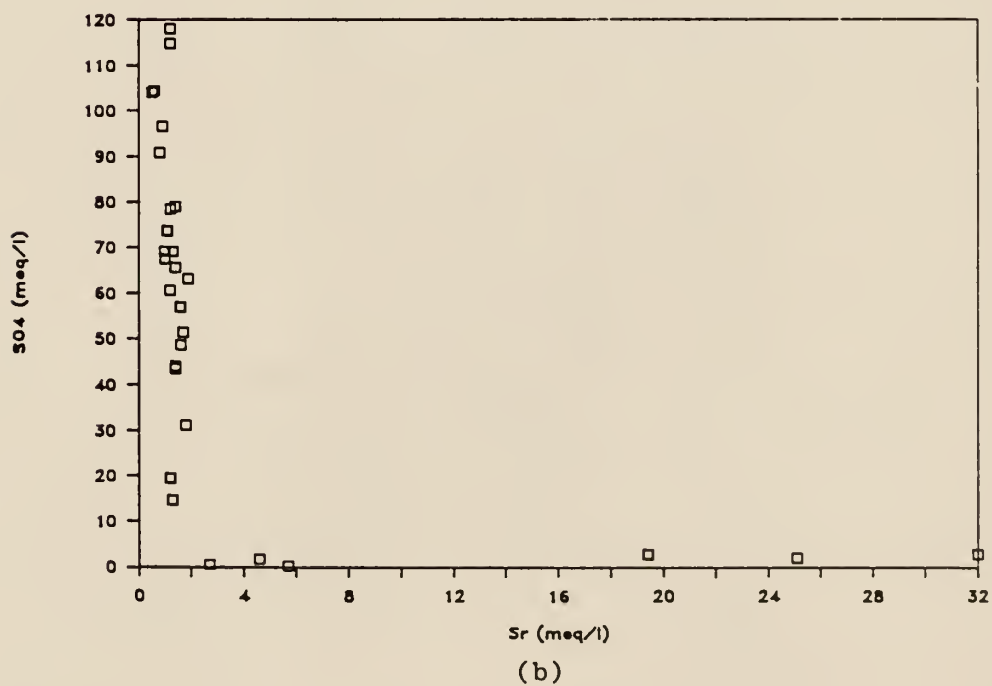
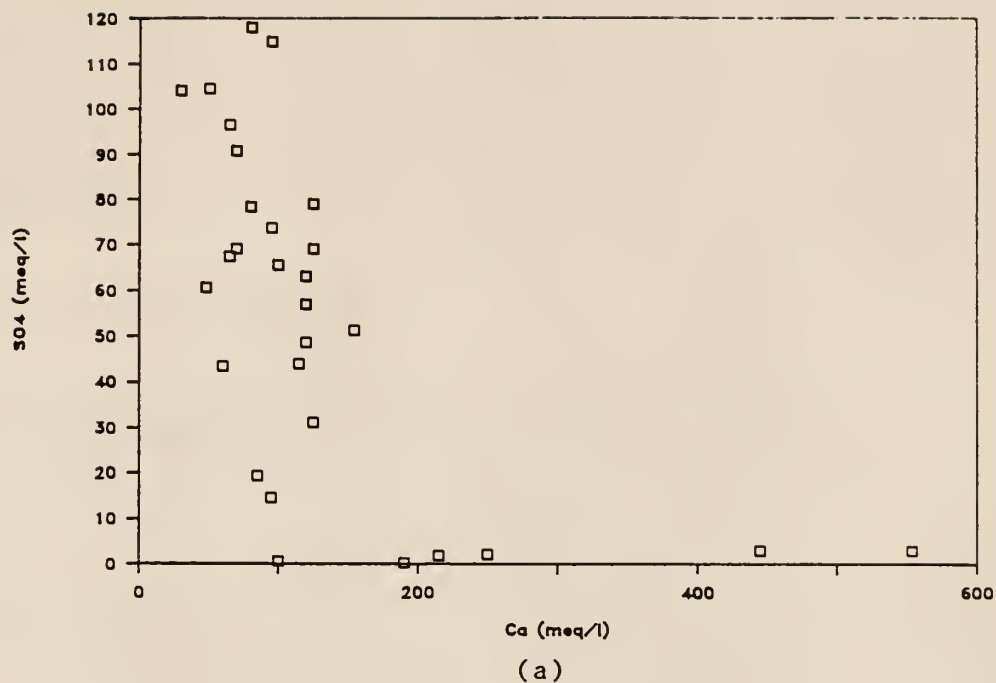


Figure 23. Concentrations of a) SO_4 vs Ca and b) SO_4 vs Sr in Lansing-Kansas City oil-field waters (concentrations in meq/l).

The additional SO_4^{2-} needed for this reaction to continue could come from dissolution of gypsum or anhydrite, which could explain the excess Ca and Sr while bacterial reduction of sulfate occurred. The Sr isotopic data, discussed below, provide some support for the dissolution of marine sulfate followed by bacterial reduction of the sulfate.

Sulfate reduction is generally greatest where meteoric water carrying bacteria enters oil-field water. In the presence of Fe^{2+} this reaction is accompanied by precipitation of iron sulfides represented by the reaction:



Pyrite was present in core sample 5 taken from the northern edge of the study area, which may suggest that SO_4 has been reduced at least locally. This process appears to be the best explanation for SO_4 depletion in the waters that are not highly Ca and Sr enriched, as these ions would not be affected by the reduction reaction.

Drever (1982) discusses a process by which the Ca(Sr)- SO_4 relationships of many of the waters could also be obtained. Figure 24 displays the Ca increase and SO_4 decrease in water produced by gypsum precipitation when the initial molar concentration of Ca is much greater than that of SO_4 . In this manner, high Ca and Sr enrichment accompanied by SO_4 depletion can be achieved by evaporation of water

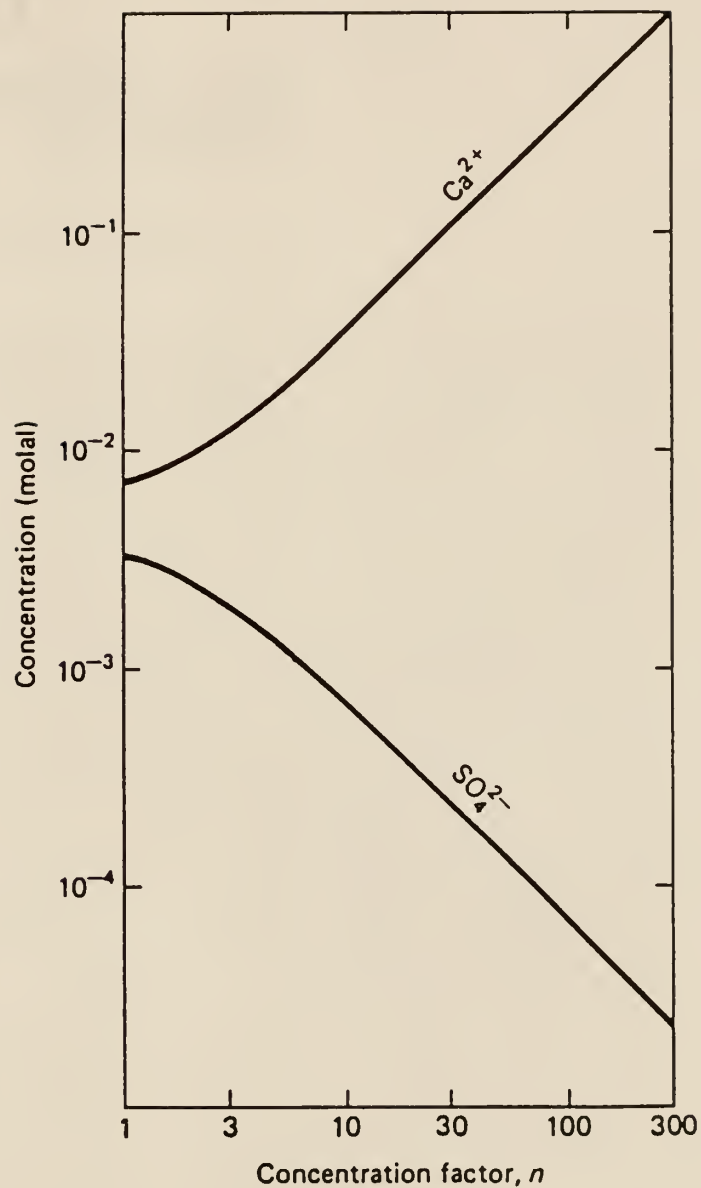


Figure 24. Concentration of Ca and SO_4 during evaporation of a solution in equilibrium with gypsum, assuming initial molar concentration of Ca is much greater than that of SO_4 , neglecting activity corrections. (from Drever, 1982).

resulting in gypsum precipitation. The influence of evaporation appears unsupported by the isotopic data, which are discussed below.

Bicarbonate

The analysis of HCO_3 was performed in the laboratory sometime after collection and the values reported here may not be accurate. However, the average HCO_3 content of the oil-field water samples (230 mg/l) is close to the mean HCO_3 content of Lansing-Kansas City oil-field waters (204 mg/l) reported by Dingman and Angino (1969).

Iodide

Iodide concentrations in the oil-field waters appear to be enriched relative to the I content in sea water. Iodide is concentrated by marine fauna and flora where it is preserved due to rapid sedimentation rates. The I is organically bound in, or adsorbed on the sediment until leached by organic salts and CaCl_2 into the associated waters (Collins, 1969). This process may account for the observed I enrichment in the water samples with the higher I concentrations, such as that found in BC-1, being due to a greater degree of I concentration in the organisms or amount of subsequent leaching.

Summary Of Processes Controlling The Major Chemistry

The chemistry of the Lansing-Kansas City oil-field waters can best be explained by a series of processes. Mixing highly evaporated sea water with much less evaporated sea water or meteoric water

produced Na depletion, Ca depletion, Sr depletion, Br enrichment, Li enrichment, and Rb enrichment. Dissolution of recrystallized halite has resulted in Br depletion and Na/Cl ratios of approximately 1. Dolomitization of carbonate reservoir rocks has produced Mg depletion, Ca and Sr enrichment, and possibly Li enrichment. Additional Sr enrichment may have been produced by the conversion of anhydrite to gypsum. The formation of illite from kaolinite, or the formation of K-feldspar from kaolinite produced K and Rb depletion and Li enrichment. Reduction of sulfate produced SO_4 depletion.

OXYGEN AND HYDROGEN ISOTOPES OF THE OIL-FIELD WATERS

The origin of oil-field waters may be traced through analyses of the oxygen and hydrogen isotopic compositions of the waters. The isotopic compositions depend not only on the source of the waters, but also on subsequent modification that may have occurred since the deviation from their sources.

The source of oil-field waters has been attributed to either sea water evaporated to different degrees or local meteoric water (Carpenter, 1978; Clayton et al., 1966; Hitchon et al., 1971; Kharaka et al., 1973). Modifications of the source isotopic characteristics can occur by such processes as: 1) evaporation, 2) isotopic exchange between the water and different minerals, 3) dissolution of different minerals, 4) waters derived from hydrous minerals during conversion to an anhydrous phase, 5) exchange with organic constituents, or 6) mixing with waters having different isotopic composition.

The use of stable isotopes to determine the evolution of oil-field water from a sea water origin requires an assumption that sea water has remained constant in its isotopic composition throughout the Phanerozoic. Muehlenbachs and Clayton (1976) believe that the O-isotope composition of Phanerozoic sea water has been buffered by sea water-oceanic crust exchange at approximately 0 per mil. Because the isotopic composition of sea water appears to have remained nearly constant throughout the Phanerozoic, the isotopic composition of the oil-field waters may be compared with that of modern sea water having $\delta D=0$ and $\delta^{18}O=0$ (Craig, 1961a).

Comparing oil-field water to meteoric water requires knowledge of the relationship between δD and $\delta^{18}O$ values of meteoric waters. Craig (1961b) noted that the δD and $\delta^{18}O$ values of meteoric waters may be expressed as:

$$\delta D = 8\delta^{18}O + 10.$$

The meteoric water line (Fig. 25) defined by this equation is primarily a function of latitude and altitude. The isotopic composition of oxygen and hydrogen in continental meteoric waters is closest to zero at the equator and gradually decreases toward the poles where it becomes highly negative.

The sea water isotopic values, the meteoric water line, and the local meteoric water value for the oil-field, based on the analysis of a water sample from Riley County, Kansas, are presented in Figure 25. Also shown is the isotopic composition of the water of crystallization in gypsum. This is a potential source of the oil-field waters because Permian salt beds containing gypsum and anhydrite are present in the

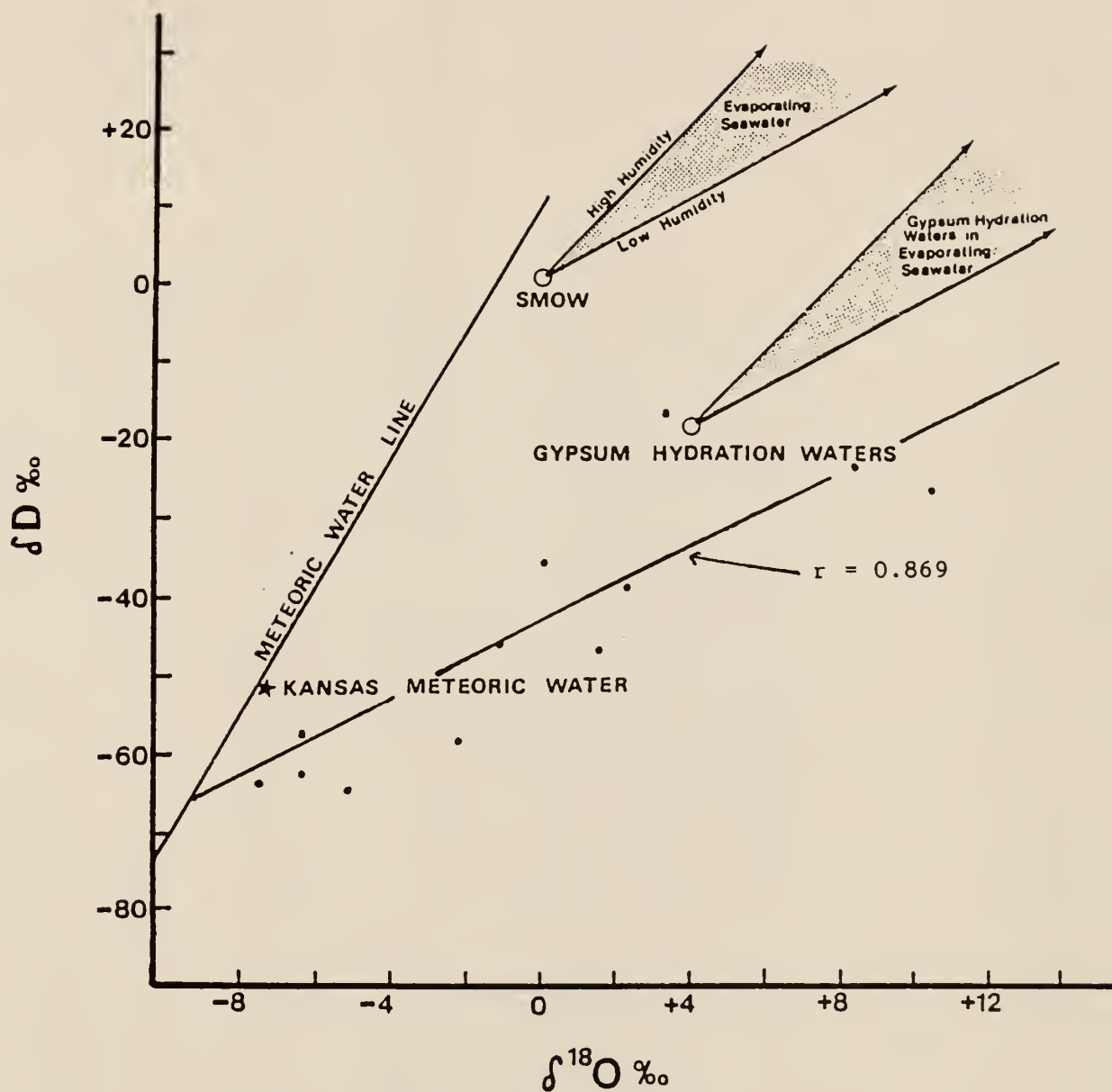


Figure 25. Relation of δD and $\delta^{18}O$ in Lansing-Kansas City oil-field waters, western Kansas to O and D shifts exhibited during evaporation of normal sea water containing hydration waters of gypsum (modified from Sofer, 1975).

subsurface of western Kansas (Zeller, 1968). Water is given off when gypsum converts to anhydrite by means of dehydration. At the time of primary gypsum precipitation, the equilibrium isotope fractionation factors (α) of O and H isotopes for the water of crystallization in gypsum at 40 °C are $\alpha^{18}\text{O} = 1.0040$ and $\alpha^{\text{D}} = 0.980$ (Sofer, 1978). The fractionation causes the water produced from the crystallization of gypsum to be enriched in ^{18}O by +4 Per mil and depleted in D by -20 per mil relative to sea water.

The effects of evaporation on the O and D isotopes of these waters can also be seen in Figure 25. The evaporation of water increases the O- and D-isotopic composition of the residual water. According to Sofer (1978), the slope of the $\delta^{18}\text{O}/\delta\text{D}$ line for the evaporation of sea water is dependent on humidity. Under dry conditions the slope is approximately 2, while humid conditions cause the value to be approximately 5.

The isotopic compositions of the Lansing-Kansas City oil-field waters are plotted on Figure 25. This array of points for the oil-field waters forms a line with a correlation coefficient (r) of 0.8690 which is significant at the 99 percent confidence level. Thus, the waters may be related by mixing of two waters, possibly a diagenetically modified evaporated sea water and continental meteoric water which have different isotopic compositions. The composition of the meteoric water component may be defined by extending the best-fit line through the data points to intercept the meteoric water line.

Evidence for meteoric water influence exists in the Lansing-Kansas City strata. Secondary porosity in rocks of the Lansing-Kansas

City Groups from northern Kansas has been attributed to meteoric water influx (Heckel, 1977, 1984, 1985, and 1986; Watney, 1980 and 1985). Solution cavities are present within the sampled carbonates of Lansing-Kansas City strata from this area. These contain zoned cements composed of ferroan calcite with non-ferroan calcite present in the center. Ferroan calcite is precipitated in an anaerobic environment which most likely occurred after burial. The non-ferroan calcite, possibly indicating aerobic conditions, was deposited later. Influx of meteoric water might have been a cause for precipitation of the non-ferroan calcite.

The intercept of the best-fit line to the meteoric water line defines the meteoric water component with δD value of about -66 per mil and $\delta^{18}O$ value of about -9 per mil. This meteoric water has δD and $\delta^{18}O$ values which are somewhat lower than present-day local meteoric water, with a δD value of about -53 per mil and a $\delta^{18}O$ value of about -7 per mil. As stated previously, latitude and altitude are the major controls on D- and O-isotopic composition of meteoric waters. Kansas has remained at nearly the same latitude throughout the Phanerozoic. Therefore, altitude and cold climate most likely determined the low δD and $\delta^{18}O$ values of the past meteoric water in Kansas. Any evidence for significant difference in altitude since the deposition of the Lansing-Kansas City sediments could not be found in the geologic record. Periods of cold climate are known to have existed during Pleistocene time when the local meteoric waters could have had isotopic compositions more negative than those of the present

time. Also, a somewhat colder climate in the pre-Pleistocene time than in the present time cannot be altogether ruled out.

The second component of the mixing model must have had δD and $\delta^{18}O$ values of greater than -20 and +12 per mil, respectively, as suggested by the values for the most enriched water samples. The isotopic composition of this end member remains ill defined because the best-fit line intersects neither the sea water evaporation field nor the gypsum water crystallization field. Apparently, lack of any relation of this second component with the sea water or the gypsum water would suggest that these waters are strongly diagenetically modified. Reactions of these waters with marine carbonate rocks, such as during dolomitization or dissolution of carbonate rocks, enriching the waters in ^{18}O , could account for the evident departure of the isotopic composition of the second component from those of sea water or gypsum waters.

Some of the water samples have δD values close to that of gypsum hydration waters (samples BC-8, BC-15, and M-1; Fig. 25), suggesting a potential contributor to the waters in the Lansing-Kansas City rocks. Sea water or evaporated sea water could contribute to the oil-field waters, which, when combined with a mixture of meteoric water and gypsum hydration water could result in values similar to those observed. The presence of evaporated sea water may also be possible because such highly saline water passing through gypsum can convert it to anhydrite. This conversion is due to the low activity of highly saline water. Hence, a mixture of meteoric water, gypsum hydration

water, and sea water or evaporated sea water can best explain the stable isotopic compositions of the water samples.

Summary of Processes Controlling the Stable Isotopic Compositions

The O- and D-isotopic composition of the oil-field waters indicates mixing of a past meteoric water, gypsum hydration water, and sea water or evaporated sea water, in varied amounts, undergoing subsequent reaction with carbonate minerals.

STRONTIUM ISOTOPES

The Lansing-Kansas City oil-field water samples have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between 0.70880 and 0.71506 (Table 9). Many of these values are higher than that of modern sea water (0.7091) and most values are above the Pennsylvanian sea water values (0.7080 - 0.7086; Burke et al., 1982). There are few published $^{87}\text{Sr}/^{86}\text{Sr}$ values for Paleozoic carbonate rocks from western Kansas. Taking the values that have been reported in the literature as being representative of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the Paleozoic rocks in Kansas, we can safely assume that Kansas carbonates have $^{87}\text{Sr}/^{86}\text{Sr}$ values less than 0.710 (Robinson, 1983). According to Chaudhuri et al. (1987) dolomitization of marine carbonate rocks would probably release Sr with a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of around 0.707 - 0.709 to the waters, and thus dolomitization would probably keep the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the waters within the range of sea water values. Hence, the process of dolomitization, which has been proposed to explain the Ca-Mg-Sr relationships of the oil-field

waters alone, cannot account for the $^{87}\text{Sr}/^{86}\text{Sr}$ values of many of the oil-field waters.

Clayton (1986) studied Permian evaporites in western Kansas and determined their $^{87}\text{Sr}/^{86}\text{Sr}$ ratio to range between 0.7081 and 0.7089. A considerable portion of the TDS of the oil-field waters may be attributed to dissolution of Permian halite, which has been suggested to explain the Br depletion of the waters. However, the high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the oil-field waters (>0.709) cannot be explained by halite dissolution.

The high $^{87}\text{Sr}/^{86}\text{Sr}$ values of several water samples require introduction of radiogenic ^{87}Sr from sources with high Rb/Sr ratios. Two potential sources of this radiogenic Sr in sedimentary rocks are clay minerals and feldspar. Shales dominate the Lansing-Kansas City Group lithology. Thus, clay minerals are potentially contributors of radiogenic Sr. Illite and illite-smectite mixed-layer clay minerals make up as much as 90 percent of the total amount of clay minerals in these shales (Table 10). Chaudhuri and Brookins (1978) reported that illite and illite-smectite mixed layer clays, because of their generally high Rb/Sr values, can have exchangeable Sr as high as 0.7277. Thus, high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (>0.710), of some oil-field waters could have resulted from Sr exchange with clay minerals in adjacent shales.

One sample (BC-1) has a much higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (0.71506) than all the others. The high value, considered to be anomalous relative to all others, may have formed from cross-formational flow of waters from underlying units. High $^{87}\text{Sr}/^{86}\text{Sr}$ waters have been

discovered in the underlying Middle Pennsylvanian Cherokee Sandstone (0.7254 - 0.7277; Nicastro, 1983) and Upper Mississippian Warsaw Limestone (0.7231 - 0.7254; Broedel, 1983). Cross-formational flow of ^{87}Sr enriched waters from the underlying Mississippian-Pennsylvanian units to the Lansing-Kansas City unit in this locality could account for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of water BC-1.

No correlation appears to exist between the high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and the K content of the waters. Correlation between K depletion and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios might occur if the illitization of smectite were a major factor for the K depletion of the waters. The Sr-isotopic variation among different production zones within the Lansing-Kansas City Groups was also investigated. Though the sample size was limited, no apparent trend could be seen relating the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and any particular production zone (Table 9). The Sr isotopic values were not uniform throughout the study area. Significant differences in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios exist among waters from adjacent wells, suggesting that isolated pockets of fluid exist in Lansing-Kansas City Groups that are not hydrologically connected.

A paradoxical situation arises when comparing the stable isotopic data with the Sr isotopic data. Many of the Lansing-Kansas City oil-field water characteristics have been explained by a process of mixing waters of different origins. The stable isotopes of O and D indicate two sources of water and hence two potential sources of Sr: 1) diagenetically modified water possibly of sea water or gypsum hydration water origin and 2) continental meteoric water. If these were the only sources of Sr, the $^{87}\text{Sr}/^{86}\text{Sr}$ vs Cl and $^{87}\text{Sr}/^{86}\text{Sr}$ vs $1/\text{Sr}$

(Fig. 26) plots would be dominated by a two component mixing relationship and thus, should show strong linear correlations, similar to the $\delta^{18}\text{O}$ vs δD plot (Fig. 25). As no trend is found in the Sr-isotopic data, at least one additional source of Sr must also be affecting the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the waters and thus producing the observed scatter. Hence, the Sr isotopic data reflects a process that is not detected by the stable isotopic data. The scatter of the data indicates a localized effect on the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. This could be due to cross-formational flow in isolated areas. Another possible cause for the scatter could be reaction with carbonate reservoir rocks having varied Sr contents and Sr isotopic compositions.

Summary of Strontium Isotopic Data

The Sr-isotopic composition of the oil-field waters has most likely been determined by mixing of marine Sr with non-marine Sr enriched in radiogenic ^{87}Sr possibly due to reaction with clay minerals. The data collected do not distinguish any isotopic difference between the production zones within the Lansing-Kansas City Groups. In some isolated pools, mixing with higher $^{87}\text{Sr}/^{86}\text{Sr}$ waters, such as those derived from Upper Mississippian or Middle Pennsylvanian rocks, may have caused the $^{87}\text{Sr}/^{86}\text{Sr}$ of the Lansing-Kansas City waters to be increased. Localized reaction with reservoir rocks could have also influenced the Sr isotopic composition of the waters.

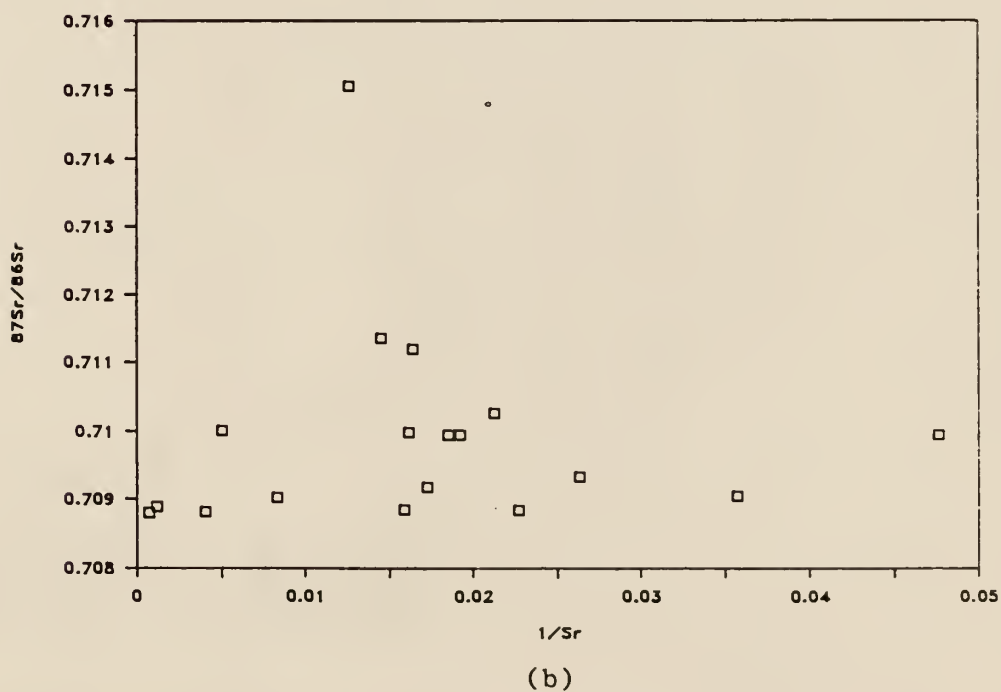
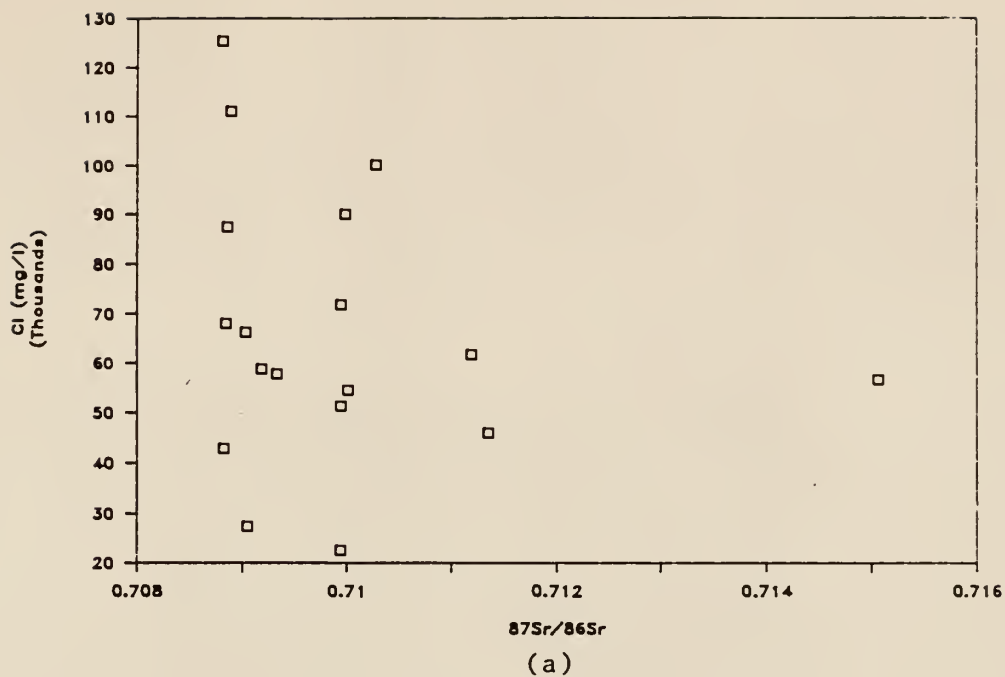


Figure 26. Relationships among chemical and isotopic characteristics of Lansing-Kansas City oil-field waters: a) Cl vs $^{87}\text{Sr}/^{86}\text{Sr}$ and b) $^{87}\text{Sr}/^{86}\text{Sr}$ vs $1/\text{Sr}$.

SPATIAL DISTRIBUTION OF WATER COMPOSITION

The TDS content of the Lansing-Kansas City oil-field waters varies greatly over western Kansas. Though data is limited, one possible distribution has been constructed (Fig. 22). This shows high concentrations of TDS in the northcentral and southern portions of the study area and low concentrations in the northwestern and eastern portions. One possible explanation for the areas of low TDS is that the oil-field waters in these areas have been diluted by low TDS waters such as meteoric water. The addition of meteoric water would cause the δD and $\delta^{18}O$ values of the oil-field water to be decreased. The geographic distribution of the δD and $\delta^{18}O$ values can be seen in Figure 21. The more negative δD and lower $\delta^{18}O$ values generally occur in the same areas as the low TDS concentrations. Also, the lowest concentrations of Ca, Mg, Sr, and K occur in these regions (Fig. 14; Fig. 17). Thus, dilution by meteoric water along the east and northwest margins of the study area may have affected the chemistry of the oil-field waters in these locations.

The geographic distribution many of the chemical characteristics of the waters shows an anomalous region present in Gove and Lane Counties. There is considerable variation in the Sr and Na concentrations in this area and extreme variation in the K concentrations (Fig. 14; Fig. 17). The δD data do not show any anomalous values in this area (Fig. 21). Thus, the influence of meteoric water is most likely not the cause of the observed chemical variation. The potentiometric data (Fig. 22) indicate an area of

lower pressure in this location. Therefore, the variation of the water composition could be due to cross-formational flow.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are highest in a band trending northwest to southeast across the study area which is located north of an area of lower pressure. This may be a location of cross-formational flow where waters from underlying formations, with higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, are increasing the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the Lansing-Kansas City waters.

The waters having the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are from the southern portion of the study area. These waters are also the most enriched in Ca and Sr and the most depleted in SO_4 . This relationship has been attributed to dissolution of gypsum or anhydrite from within the Permian evaporites, followed by reduction of SO_4 . This dissolution would release Sr to the waters having the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the Permian evaporites (0.7081 - 0.7089; Clayton, 1986). Since the waters in this area have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios within the range of values for Permian evaporites, the dissolution of gypsum or anhydrite could be controlling the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the waters in this area.

The eastern margin of the study area is close to the Central Kansas Uplift. As mentioned above, the early Pennsylvanian activity of this structure, caused pre-Pennsylvanian strata to be upturned and truncated on the flanks of the uplift. The Lansing-Kansas City Groups were deposited over the deformed strata and are underlain by successively younger units from the crest of the uplift, toward the west. The possibility of the formation below the Lansing-Kansas City Group exerting some control on the chemistry of the Lansing-Kansas City water, through cross-formational flow, was investigated. There

is no apparent correlation between underlying formation and the chemical or isotopic composition of the Lansing-Kansas City waters.

CONCLUSION

The following conclusions may be drawn as a result of this study. Four of the oil-field waters are classified as chloride-magnesium type. These waters are from the northeastern and northwestern portions of the study area where meteoric water influx has diluted the waters within the Lansing-Kansas City Groups. The remaining waters are chloride-calcium type. The processes controlling the water chemistry appear to be similar for both water types. The major chemical data are explained by: a) mixing of highly evaporated sea water with much less evaporated sea water or meteoric water, b) dissolution of recrystallized halite and anhydrite-gypsum in evaporite sequences, c) dolomitization of carbonate reservoir rocks, and d) formation of secondary minerals such as illite and alkali feldspar. The O and D stable isotopic data can best be explained by mixing of meteoric water and sea water or evaporated sea water, or even gypsum hydration water, followed by varied amounts of reactions with carbonate minerals. The Sr-isotopic composition of the oil-field waters indicates that radiogenic ^{87}Sr has been added in varying amounts to marine Sr. The source of the marine Sr could be both the meteoric water component and the sea water component. The radiogenic ^{87}Sr was possibly derived from reactions with clay minerals. Cross-formational flow of waters enriched in ^{87}Sr is a strong possibility for a few of the water

samples, especially in the central part of the study area. In general, the water samples more to the south have Sr isotopic compositions, with low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, that are similar to the values of marine Sr. These waters also have high salinities. Thus, the Sr isotopic data are reflections of evaporated sea water and of dissolution of minerals in the evaporitic sequence. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of waters from adjacent wells are often varied, suggesting the presence of locally isolated pockets of fluids. In this study, no definite chemical or isotopic criteria can be used to determine the contribution to the waters from the different production zones within the Lansing-Kansas City Groups or any particular underlying formation. Spatial distribution of the chemical and isotopic composition of the waters indicate a meteoric water influence in the northeast and northwest portions of the study area which was probably associated with the meteoric water diagenesis observed in the Lansing-Kansas City strata in these areas.

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CHEMICAL EVOLUTION OF WATERS IN THE LANSING-KANSAS CITY GROUPS
IN WESTERN KANSAS

by

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ABSTRACT

Chemical and isotopic characteristics of oil-field waters associated with the Upper Pennsylvanian Lansing-Kansas City Groups in western Kansas were determined to test the origin and chemical history of the fluids. The majority of the waters were chloride-sodium-calcium type, having salinities between 41,000 and 217,000 mg/l. The salinities were higher in the northcentral and southern portions of the study area. The Na concentration ranged from 17,000 to 60,000 mg/l and the Cl concentration ranged from 23,000 to 125,000 mg/l. Compared to sea water at their equivalent Cl contents, typically these waters are deficient in Mg (120-2,700 mg/l), K (<30-800 mg/l), Br (33-450 mg/l), and SO_4 (16-5,670 mg/l) and are mostly enriched in Ca (600-11,100 mg/l), Sr (21-1,400 mg/l), Li (1.9-8.8 mg/l), and Rb (0.1-0.6 mg/l). The Na/Cl ratio of most of the waters was either similar to evaporating sea water or close to that of halite. The δD values of the oil-field waters were between -58 and -16 per mil and the $\delta^{18}\text{O}$ values between -1.1 and +10.3 per mil, relative to SMOW. Mixing of meteoric water with sea water or evaporated sea water along with dolomitization, illitization, and dissolution of evaporitic deposits were the most likely processes affecting the chemical and stable isotopic compositions of the oil-field waters.

Seventeen out of 20 of the waters had $^{87}\text{Sr}/^{86}\text{Sr}$ values between 0.7088 and 0.7102. The three exceptions had $^{87}\text{Sr}/^{86}\text{Sr}$ values between 0.7111 and 0.7150. The Sr isotopic data suggest that isolated pools of fluid exist within the Lansing-Kansas City carbonate reservoirs and that mixing with fluids from lower units may occur in the central

portion of the study area. The Sr isotopic compositions of the waters from the southern portion of the study area are dominated by marine Sr possibly due to the dissolution of Permian evaporites by evaporated sea water.

No definite chemical or isotopic criteria can be used to determine the contribution to the waters from the different production zones within the Lansing-Kansas City Groups or any particular underlying formation. Spatial distribution of the chemical and isotopic composition of the waters indicate a meteoric water influence in the northeast and northwest portions of the study area which was probably associated with the meteoric water diagenesis observed in the Lansing-Kansas City strata in these areas.